STATEMENT

I, Naoshi KITAMURA—of Toranomon East Bldg. 7-13, Nishi-Shimbashi 1-chome, Minato-ku, Tokyo 105-8408 Japan—hereby declare that I am conversant in both Japanese and English and that I believe the following is true and correct translation of Japanese Patent Application No. 2003-082852.

Date: June 16, 2006

Naoshi KITAMURA

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Applicant: FUJI PHOTO FILM CO., LTD.

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[Designation of Document] Specification

[Title of the Invention] Inkjet Ink and Inkjet Ink Set

[Scope of Claims for Patent]

[Claim 1] An inkjet ink comprising at least one dye in an aqueous medium, wherein the dye satisfies a relation of $\varepsilon 1/\varepsilon 2 > 1.2$ wherein $\varepsilon 1$ represents a molar extinction coefficient obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.1 mmol/liter using a cell having a light pass length of 1 cm and $\varepsilon 2$ represents a molar extinction coefficient obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.2 mmol/liter using a cell having a light pass length of 5 μm.

[Claim 2] An inkjet ink set comprising the ink as claimed in Claim 1 as at least one of constituting inks.

[Claim 3] The inkjet ink set as claimed in Claim 2, wherein the dye contained in the ink as claimed in Claim 1 constituting the ink set is an azo dye having a heterocyclic group.

[Claim 4] The inkjet ink set as claimed in Claim 3, wherein the azo dye having a heterocyclic group is an azo dye wherein two heterocyclic groups are connected by an azo bond.

[Claim 5] The inkjet ink set as claimed in Claim 2, wherein the dye contained in the ink as claimed in Claim 1 constituting the ink set is a metal chelate dye wherein a metal coordinated with a heterocyclic group forms a nucleus.

[Claim 6] The inkjet ink set as claimed in Claim 5, wherein the metal chelate dye wherein a metal coordinated with a heterocyclic group forms a nucleus is a phthalocyanine dye.

[Detailed Description of the Invention]

[Technical Field to which the Invention Belongs]

The present invention relates to an inkjet ink and an inkjet ink set, which forms an image having excellent durability.

[Technical Background of the Invention]

With the popularization of computers in recent years, inkjet printers are widely used not only at offices but also at homes for printing letters or images on paper, films, cloths or the like.

The inkjet recording method includes a system of ejecting a liquid droplet upon applying a pressure by means of a piezoelectric element, a system of ejecting a liquid droplet by generating a bubble in an ink upon heat, a system of using an ultrasonic wave, and a system of ejecting a liquid droplet by drawing with an electrostatic force. An ink composition for use in such inkjet recording methods includes an aqueous ink, an oily ink and a solid (melt-type) ink. Of these inks, the aqueous ink becomes mainstream in view of production, handleability, odor, safety and the like.

A coloring agent used in such an ink for inkjet recording method is required to have high solubility in a solvent, enable high-density recording, have good color hue, exhibit excellent fastness

to light, heat, air, water and chemicals, ensure good fixing property and less bleeding on an image-receiving material, provide an ink having excellent preservability, shows no toxicity, have high purity, and be available at a low cost. However, it is very difficult to find out a coloring agent satisfying these requirements at a high level. Although various dyes and pigments for inkjet recording have been already proposed and practically used, a coloring agent satisfying all of such requirements is not yet found out at present. Conventionally well-known dyes and pigments, for example, those having a Colour Index (C.I.) number can hardly satisfy both the color hue and fastness required to the ink for inkjet recording.

The inventors have made technical searches for resolving the above-described problems existing in the inkjet ink using dye and found that an aqueous inkjet ink is many times particularly inferior in image durability due to the water solubility. As dyes suitable for the aqueous inkjet ink, azo dyes containing a heterocyclic group having a specific structure are disclosed in Patent Document 1 described below, and phthalocyanine dyes having specific structures are disclosed in Patent Documents 2 to 4 described below. These techniques exhibit improvements in simultaneous pursuit of the color hue and fastness. However, further improvements have been desired in order to use inkjet recording images under various environments in doors and out of doors.

Patent Document 1: JP-A-2002-371214

Patent Document 2: JP-A-2003-3086

Patent Document 3: JP-A-2003-3099

Patent Document 4: JP-A-2003-3109

[Problems that the Invention is to Solve]

An object of the present invention is to provide an inkjet ink, which is aqueous, is excellent in ejection stability at the image drawing and provides a drawing image having excellent image fastness, and to provide an inkjet ink set including the above-described ink.

[Means for Solving the Problems]

The objects of the invention can be attained by the inkjet ink described in item (1) and the inkjet ink set described in items (2) to (7) below.

(1) An inkjet ink comprising at least one dye in an aqueous medium, wherein the dye satisfies a relation of $\varepsilon 1/\varepsilon 2 > 1.2$ wherein $\varepsilon 1$ represents a molar extinction coefficient obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.1 mmol/liter using a cell having a light pass length of 1 cm and $\varepsilon 2$ represents a molar extinction coefficient obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.2 mmol/liter using a cell having a light pass length of 5 μm.

(2) An inkjet ink set comprising the ink as described in item (1) above as at least one of constituting inks.

(3) The inkjet ink set as described in item (2) above, wherein the dye contained in the ink as described in item (1) above constituting the ink set is an azo dye having a heterocyclic group.

(4) The inkjet ink set as claimed described in item (3) above, wherein the azo dye having a heterocyclic group is an azo dye wherein two heterocyclic groups are connected by an azo bond.

(5) The inkjet ink set as described in item (2) above, wherein the dye contained in the ink described in item (1) above constituting the ink set is a metal chelate dye wherein a metal coordinated with a heterocyclic group forms a nucleus.

(6) The inkjet ink set as described in item (5) above, wherein the metal chelate dye wherein a metal coordinated with a heterocyclic group forms a nucleus is a phthalocyanine dye.

(7) The inkjet ink set as described in any one of items (2) to (6) above, wherein the dye contained in the ink as described in item (1) above is a dye having an oxidation potential more positive than 1.0 V (vs SCE).

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

The ink in the ink set of the invention comprises at least one dye dissolved or dispersed in an aqueous medium, and at least one dye contained in the ink has a property of forming association in a concentrated ink solution and decreasing an apparent molar extinction coefficient (ε) in comparison with a diluted ink solution.

The dye having such a property is characterized by exhibiting concentration dependency of the molar extinction coefficient in an aqueous solution as described below. Specifically, the dye satisfies the following relation between a molar extinction coefficient (ε1) obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.1 mmol/liter using a cell having a light pass length of 1 cm and a molar extinction coefficient (ε2) obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.2 mmol/liter using a cell having a light pass length of 5 μm.

More specifically, two or more molecules of the dyes for use in the invention are associated in a solution having high concentration and exhibit a behavior as if molar extinction coefficient of the dye decreases in comparison with in a diluted solution. Therefore, the dye has the feature that as the concentration increases, it behaves as if apparent absorbance compensated by the concentration of solution decreases. The absorbance of dye in a diluted solution can be measured using a conventional cell. However, in order to measure the absorbance of dye in a solution having high concentration as in the invention, a cell having a very short light pass length is necessary. Thus, a liquid crystal cell is employed for such a purpose in the invention and the value thus-obtained is compared with a value obtained by measuring using a cell having a long light pass length, whereby dye concentration dependency of the absorbance is determined as a scale for a characteristic of

preferred dye. The behavior of change in the ratio of molar extinction coefficient is believed to depend on difference in association degree of the dye. The dye having the ratio of molar extinction coefficient of 1.2 or more exhibits remarkable image fastness suiting the purpose of the invention. The upper limit of the ratio of molar extinction coefficient is not particularly limited as far as the absorbance of the concentrated solution extremely decreases, but is ordinarily 3 or below.

The term "liquid crystal cell" as used herein includes a measurement cell having a light pass length similar to the liquid crystal cell as is apparent from the above-described purport and should not be construed as being limited to the liquid crystal cell alone.

Of the dyes for use in the inkjet ink and inkjet ink set according to the invention, those having an oxidation potential more positive than 1.00 V (vs SCE) in addition to the above-described properties are preferably used because they exhibit excellent effects. The dyes having an oxidation potential more positive than 1.10 V (vs SCE) are more preferable, the dyes having an oxidation potential more positive than 1.20 V (vs SCE) are still more preferable, and the dyes having an oxidation potential positive than 1.25 V (vs SCE) are the most preferable.

Any dye can be used in the invention as long as the dye satisfies the above-described property regarding the dye concentration dependency of the molar extinction coefficient. The dye preferably used in the invention can be selected from the azo dye, the metal chelate dye and the phthalocyanine dye as described in item (2) to (6). More specially, the dye preferably can be selected from the dye represented by formulae (1) to (4) as the below-described.

Thus, more preferred dyes are dyes selected from the dyes represented by any one of formulae (1) to (4) and having an oxidation potential more positive than 1.00 V (vs SCE).

Examples of the measurement method of the oxidation potential include, for an aqueous solution or mixed solvent system in which a dye is dissoloved, a polarography method, a cyclic voltammetri (CV) method, a ring disc-rotating electrode method, a comb electrode method, and the like. More specifically, a test sample is dissolved at a concentration of 1×10^{-6} to 1×10^{-4} mol/liter in a solvent, for example, dimethylformamide or acetonitrile containing a supporting electrolyte, for example, sodium perchlorate or tetrapropylammonium perchlorate and the oxidation potential is measured as a value to SCE (saturated calomel electrode) using a cyclic voltammetry. The supporting electrolyte and solvent to be used may appropriately be selected according to the oxidation potential or the solubility of the subject. The supporting electrolyte and solvent to be used are disclosed in Akira Fujishima et al., Denkikagaku Sokuteiho (Electrochemical Measuring Methods), pages 101-118, Gihodo Shuppan Co., Ltd. (1984).

The value of the oxidation potential sometimes may deviate on the order of several tens of millivolts due to the effect of liquid junction potential, liquid resistance of the sample solution or the like, however, reproducibility of the potential can be guaranteed using a standard sample (for example, hydroquinone).

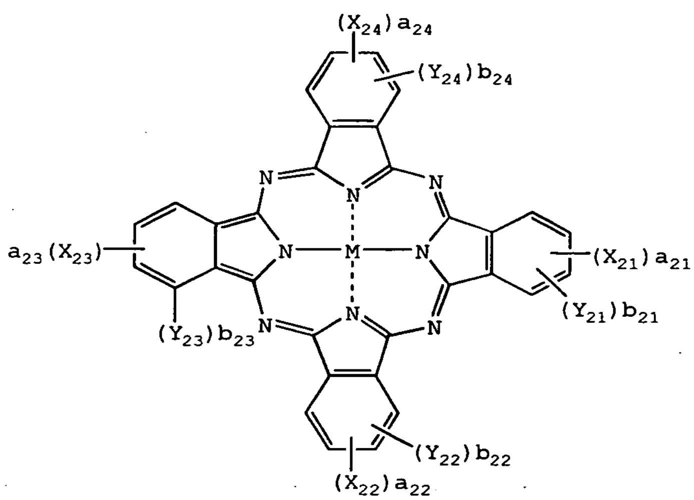
As the oxidation potential, a value (vs SCE) measured by the direct-current polarography using a saturated calomel electrode as a reference electrode, a graphite electrode as a working electrode, and an N,N- dimethylformamide solution (concentration of dye: 0.001 mol dm^{-3}) containing 0.1 mol dm^{-3} of tetrapropylammonium perchlorate as the supporting electrolyte is used as the oxidation potential of the dye.. In the case of a water-soluble dye, the dye is sometimes hardly dissolved directly in N,N-dimethylformamide. In such a case, the oxidation potential is measured after dissolving the dye using water in a small amount as much as possible and then diluting the aqueous solution with N,N-dimethylformamide so as to have a water content of 2% or below.

The dyes represented by any one of formulae (1) to (4) preferably used in the invention are described below.

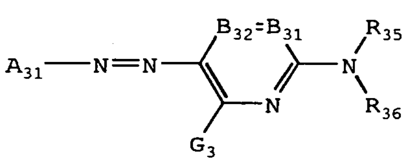
Formula (1):

$$A_{11}\text{-N=N-}B_{11}$$

Formula (2):



Formula (3):



Formula (4):

$$A\text{-(N=N-}B_m)^n\text{-N=N-C}$$

In formula (1), A_{11} and B_{11} each independently represents a heterocyclic group which may be substituted

In formula (2), X_{21}, X_{22}, X_{23} and X_{24} each independently represents -SO-Z, $-SO_2$-Z, $-SO_2NR_{21}R_{22}$, a sulfo group, $-CONR_{21}R_{22}$ or $-COOR_{21}$,

Z independently represents a substituted or unsubstituted alkyl group, a substituted or

unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group,

R_{21} and R_{22} each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group,

Y_{21}, Y_{22}, Y_{23} and Y_{24} each independently represents a monovalent substituent,

a_{21} to a_{24} and b_{21} to b_{24} represent the numbers of substituents X_{21}, X_{22}, X_{23} and X_{24} and Y_{21} Y_{22}, Y_{23} and Y_{24}, respectively, a_{21} to a_{24} each independently represents an integer of from 0 to 4, provided that all of a_{21} to a_{24} are not 0 at the same time, and b_{21} to b_{24} each independently represents an integer of from 0 to 4, provided that when a_{21} to a_{24} and b_{21} to b_{24} each represents an integer of 2 or more, the plurality of X_{21}s, X_{22}s, X_{33}s, X_{24}s, Y_{21}s, Y_{22}s, Y_{23}s or Y_{24}s may be the same or different from each other, and

M represents a metal atom or an oxide, hydroxide or halide thereof;

In formula (3), A represents a 5-membered heterocyclic group,

B_{31} and B_{32} each represents $=CR_{31}-$ or $-CR_{32}=$, or either one of B_{31} and B_{32} represents a nitrogen atom and the other represents $=CR_{31}-$ or $-CR_{32}=$,

R_{35} and R_{36} each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent,

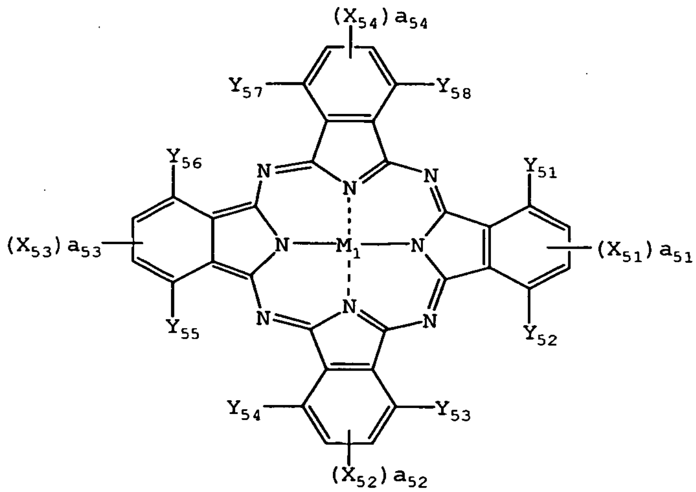
G, R_{31} and R_{32} each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxy group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group, a sulfo group or a heterocyclic thio group, and each group may be further substituted, and

R_{31} and R_{35}, or R_{35} and R_{36} may be combined with each other to form a 5-membered or 6-membered ring;

In formula (4), A, B and C each independently represents an aromatic group which may be substituted or a heterocyclic group which may be substituted. M and n each represents an integer of 0 or more.

The dye represented by formula (2) is preferably a represented by formula (5) below.

Formula (5):



In formula (5), X_{51} to X_{54}, Y_{51} to Y_{58} and M_1 have the same meanings as X_{21} to X_{24}, Y_{21} to Y_{24} and M in formula (2), respectively, and a_{51} to a_{54} each independently represents an integer of 1 or 2.

The above-described azo dye represented by formula (1), (3) or (4) and phthalocyanine dye represented by formula (2) can be used in any one of cyan ink, magenta ink, yellow ink, light cyan ink, light magenta ink, light yellow ink and black ink constituting the ink set of the invention.

When the dye is used in the black ink, among dyes represented by one of formulae (1) to (4), particularly azo dyes represented by formula (3) or (4), longer wavelength-absorbing dyes (dyes L) having λmax in the region from 500 to 700 nm and shorter wavelength-absorbing dyes (dyes S) having λmax in the region from 350 to 500 nm may be used in combination. An ink where at least one dye (L) is the dye of one of formulae (1) to (4) is preferred, an ink where at least one dye (L) and at least one dye (S) are the dye of one of formulae (1) to (4) is more preferred, an ink where 90 mass% of all dyes in the ink is occupied by the dye of formula (3) or (4) is still more preferred.

In the cyan ink, magenta ink, light cyan ink and light magenta ink, the dye being one of formulae (1) to (4) and being the longer wavelength-absorbing dye having λmax in the region from 500 to 700 nm is preferred.

As a shorter wavelength-absorbing dye in the yellow ink or dark yellow ink, the dye having λmax in the region from 350 to 500 nm, particularly being represented by one of formulae (1), (3) and (4) is preferred.

Although in the following description about the dyes of formulae (1) to (4), a dye is, for

convenience sake, classified into one of the dyes (L) and (S) and is explained, the invention is not limited to the black ink.

First, among dyes of formulae (1), (3) and (4), the dye (L) is described below.

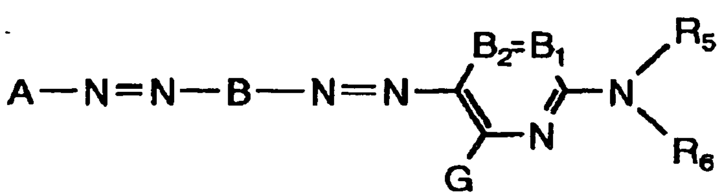
In formula (3) and (4), A, B and C each independently represents an aromatic group which may be substituted or a heterocyclic group which may be substituted (A and C are a monovalent group and B is a divalent group). m and n is an integer of 0 or more.

Among these, a compound in which each of m and n is 1 or 2 is preferred. In this case, at least two of A, B and C are preferably saturated heterocyclic groups which may be substituted. Further, the most preferable case is such a case that m=n=1 and at least B and C are saturated heterocyclic groups

Meanwhile, A^{11} and B^{11} of formula (1) each independently represents a heterocyclic group which may be substituted. In the following description below for each formula, the description of A^{11} and B^{11} is included in the description of A and C of formulae (3) and (4) since A^{11} and B^{11} have the same meanings as A and C in a case where A and C represents a heterocyclic group which may be substituted.

The azo dye represented by formula (4) is preferably a dye represented by the following formula (6):

Formula (6):



In formula (6), B_1 and B_2 each represents $=CR_1-$ or $-CR_2=$, or either one of B_1 and B_2 represents a nitrogen atom and the other represents $=CR_1-$ or $-CR_2=$,

G, R_1 and R_2 each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group, a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo

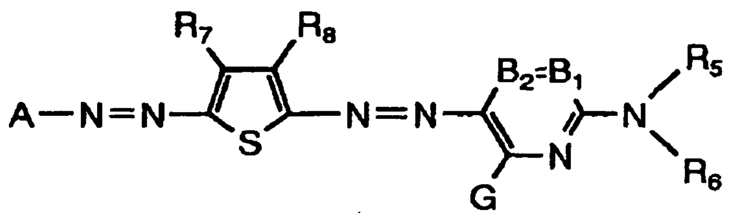
group, and each group may be further substituted,

R_5 and R_6 each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent, provided that R_{45} and R_{46} are not a hydrogen atom at the same time, and

R_1 and R_5, or R_5 and R_6 may combine to form a 5- or 6-membered ring.

The azo dye represented by formula (6) is more preferably a dye represented by the following formula (7):

Formula (7):



In formula (7), R_7 and R_8 each has the same meaning as R_1 in formula (6).

G, R_1, R_2, R_7 and R_8 of formulae (6) and (7) are further described below.

The halogen atom includes a fluorine atom, a chlorine atom and a bromine atom.

The aliphatic group means an alkyl group, a substituted alkyl group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an aralkyl group and a substituted aralkyl group. The aliphatic group may be branched or may form a ring. The number of carbon atoms in the aliphatic group is preferably from 1 to 20, more preferably from 1 to 16. The aryl moiety in the aralkyl group and the substituted aralkyl group is preferably phenyl or naphthyl, more preferably phenyl. Examples of the aliphatic group include a methyl group, an ethyl group, a butyl group, an isopropyl group, a tert-butyl group, a hydroxyethyl group, a methoxyethyl group, a cyanoethyl group, a trifluoromethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a cyclohexyl group, a benzyl group, a 2-phenethyl group, a vinyl group and an allyl group.

The monovalent aromatic group means an aryl group and a substituted aryl group. The aryl group is preferably a phenyl group or a naphthyl group, more preferably a phenyl group. The number of carbon atoms in the monovalent aromatic group is preferably from 6 to 20, more preferably from 6 to 16. Examples of the monovalent aromatic group include a phenyl group, a p-tolyl group, a p-methoxyphenyl group, an o-chlorophenyl group and an m-(3-sulfopropylamino)phenyl group. The divalent aromatic group is a divalent form of these monovalent aromatic groups and examples thereof include a phenylene group, a p-tolylene group, a p-methoxyphenylene group, an o-chlorophenylene group, an m-(3-sulfopropylamino)phenylene group and a naphthylene group.

The heterocyclic group includes a heterocyclic group having a substituent and an

unsubstituted heterocyclic group. The heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or another heterocyclic ring. The heterocyclic group is preferably a 5- or 6-membered heterocyclic group. Examples of the heteroatom in the heterocyclic ring include N, O and S. Examples of the substituent include an aliphatic group, a halogen atom, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfamoyl group, a carbamoyl group and an ionic hydrophilic group. Examples of the heterocyclic ring used in the monovalent or divalent heterocyclic group include a pyridine ring, a thiophene ring, a thiazole ring, a benzothiazole ring, a benzoxazole ring and a furan ring.

The carbamoyl group includes a carbamoyl group having a substituent and an unsubstituted carbamoyl group. Examples of the substituent include an alkyl group. Examples of the carbamoyl group include a methylcarbamoyl group and a dimethylcarbamoyl group.

The alkoxycarbonyl group includes an alkoxycarbonyl group having a substituent and an unsubstituted alkoxycarbonyl group. The alkoxycarbonyl group is preferably an alkoxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonyl group include a methoxycarbonyl group and an ethoxycarbonyl group.

The aryloxycarbonyl group includes an aryloxycarbonyl group having a substituent and an unsubstituted aryloxycarbonyl group. The aryloxycarbonyl group is preferably an aryloxycarbonyl group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aryloxycarbonyl group include a phenoxycarbonyl group.

The heterocyclic oxycarbonyl group includes a heterocyclic oxycarbonyl group having a substituent and an unsubstituted heterocyclic oxycarbonyl group. The heterocyclic oxycarbonyl group is preferably a heterocyclic oxycarbonyl group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic oxycarbonyl group include a 2-pyridyloxycarbonyl group.

The acyl group includes an acyl group having a substituent and an unsubstituted acyl group. The acyl group is preferably an acyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyl group include an acetyl group and a benzoyl group.

The alkoxy group includes an alkoxy group having a substituent and an unsubstituted alkoxy group. The alkoxy group is preferably an alkoxy group having from 1 to 20 carbon atoms. Examples of the substituent include an alkoxy group, a hydroxyl group and an ionic hydrophilic group. Examples of the alkoxy group include a methoxy group, an ethoxy group, an isopropoxy group, a methoxyethoxy group, a hydroxyethoxy group and a 3-carboxypropoxy group.

The aryloxy group includes an aryloxy group having a substituent and an unsubstituted aryloxy group. The aryloxy group is preferably an aryloxy group having from 6 to 20 carbon atoms.

Examples of the substituent include an alkoxy group and an ionic hydrophilic group. Examples of the aryloxy group include a phenoxy group, a p-methoxyphenoxy group and an o-methoxyphenoxy group.

The heterocyclic oxy group includes a heterocyclic oxy group having a substituent and an unsubstituted heterocyclic oxy group. The heterocyclic oxy group is preferably a heterocyclic oxy group having from 2 to 20 carbon atoms. Examples of the substituent include an alkyl group, an alkoxy group and an ionic hydrophilic group. Examples of the heterocyclic oxy group include a 3-pyridyloxy group and a 3-thienyloxy group.

The silyloxy group is preferably a silyloxy group substituted by an aliphatic or aromatic group having from 1 to 20 carbon atoms. Examples of the silyloxy group include a trimethylsilyloxy group and a diphenylmethylsilyloxy group.

The acyloxy group includes an acyloxy group having a substituent and an unsubstituted acyloxy group. The acyloxy group is preferably an acyloxy group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acyloxy group include an acetoxy group and a benzoyloxy group.

The carbamoyloxy group includes a carbamoyloxy group having a substituent and an unsubstituted carbamoyloxy group. Examples of the substituent include an alkyl group. Examples of the carbamoyloxy group include an N-methylcarbamoyloxy group.

The alkoxycarbonyloxy group includes an alkoxycarbonyloxy group having a substituent and an unsubstituted alkoxycarbonyloxy group. The alkoxycarbonyloxy group is preferably an alkoxycarbonyloxy group having from 2 to 20 carbon atoms. Examples of the alkoxycarbonyloxy group include a methoxycarbonyloxy group and an isopropoxycarbonyloxy group.

The aryloxycarbonyloxy group includes an aryloxycarbonyloxy group having a substituent and an unsubstituted aryloxycarbonyloxy group. The aryloxycarbonyloxy group is preferably an aryloxycarbonyloxy group having from 7 to 20 carbon atoms. Examples of the aryloxycarbonyloxy group include a phenoxycarbonyloxy group.

The amino group includes an amino group substituted by an alkyl group, an aryl group or a heterocyclic group, and the alkyl group, the aryl group and the heterocyclic group each may further have a substituent. The alkylamino group is preferably an alkylamino group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylamino group include a methylamino group and a diethylamino group.

The arylamino group includes an arylamino group having a substituent and an unsubstituted arylamino group. The arylamino group is preferably an arylamino group having from 6 to 20 carbon atoms. Examples of the substituent include a halogen atom and an ionic hydrophilic group. Examples of the arylamino group include an anilino group and a 2-chlorophenylamino group.

The heterocyclic amino group includes a heterocyclic amino group having a substituent and

an unsubstituted heterocyclic amino group. The heterocyclic amino group is preferably a heterocyclic amino group having from 2 to 20 carbon atoms. Examples of the substituent include an alkyl group, a halogen atom and an ionic hydrophilic group.

The acylamino group includes an acylamino group having a substituent and an unsubstituted acylamino group. The acylamino group is preferably an acylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the acylamino group include an acetylamino group, a propionylamino group, a benzoylamino group, an N-phenylacetylamino group and a 3,5-disulfobenzoylamino group.

The ureido group includes a ureido group having a substituent and an unsubstituted ureido group. The ureido group is preferably a ureido group having from 1 to 20 carbon atoms. Examples of the substituent include an alkyl group and an aryl group. Examples of the ureido group include a 3-methylureido group, a 3,3-dimethylureido group and a 3-phenylureido group.

The sulfamoylamino group includes a sulfamoylamino group having a substituent and an unsubstituted sulfamoylamino group. Examples of the substituent include an alkyl group. Examples of the sulfamoylamino group include an N,N-dipropylsulfamoylamino group.

The alkoxycarbonylamino group includes an alkoxycarbonylamino group having a substituent and an unsubstituted alkoxycarbonylamino group. The alkoxycarbonylamino group is preferably an alkoxycarbonylamino group having from 2 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the alkoxycarbonylamino group include an ethoxycarbonylamino group.

The aryloxycarbonylamino group includes an aryloxycarbonylamino group having a substituent and an unsubstituted aryloxycarbonylamino group. The aryloxycarbonylamino group is preferably an aryloxycarbonylamino group having from 7 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the aryloxycarbonylamino group include a phenoxycarbonylamino group.

The alkylsulfonylamino group includes an alkylsulfonylamino group having a substituent and an unsubstituted alkylsulfonylamino group, and the arylsulfonylamino group includes an arylsulfonylamino group having a substituent and an unsubstituted arylsulfonylamino group. The sulfonylamino group is preferably a sulfonylamino group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of these sulfonylamino groups include a methylsufonylamino group, an N-phenyl-methylsulfonylamino group, a phenylsulfonylamino group and a 3-carboxyphenylsulfonylamino group.

The heterocyclic sulfonylamino group includes a heterocyclic sulfonylamino group having a substituent and an unsubstituted heterocyclic sulfonylamino group. The heterocyclic sulfonylamino group is preferably a heterocyclic sulfonylamino group having from 1 to 12 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic

sulfonylamino group include a 2-thiophenesulfonylamino group and a 3-pyridinesulfonylamino group.

The heterocyclic sulfonyl group includes a heterocyclic sulfonyl group having a substituent and an unsubstituted heterocyclic sulfonyl group. The heterocyclic sulfonyl group is preferably a heterocyclic sulfonyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfonyl group include a 2-thiophene-sulfonyl group and a 3-pyridinesulfonyl group.

The heterocyclic sulfinyl group includes a heterocyclic sulfinyl group having a substituent and an unsubstituted heterocyclic sulfinyl group. The heterocyclic sulfinyl group is preferably a heterocyclic sulfinyl group having from 1 to 20 carbon atoms. Examples of the substituent include an ionic hydrophilic group. Examples of the heterocyclic sulfinyl group include a 4-pyridinesulfinyl group.

The alkylthio group includes include an alkylthio group having a substituent and an unsubstituted alkylthio group, the arylthio group includes an arylthio group having a substituent and an unsubstituted arylthio group, and the heterocyclic thio group includes a heterocyclic thio group having a substituent and an unsubstituted heterocyclic thio group. The alkylthio group, the arylthio group and the heterocyclic thio group are preferably an alkylthio group having from 1 to 20 carbon atoms, an arylthio group having from 1 to 20 carbon atoms and a heterocyclic thio group having from 1 to 20 carbon atoms, respectively. Examples of the substituent include an ionic hydrophilic group. Examples of the alkylthio group, arylthio group and heterocyclic thio group include a methylthio group, a phenylthio group and a 2-pyridylthio group.

The alkylsulfonyl group includes an alkylsulfonyl group having a substituent and an unsubstituted alkylsulfonyl group, and the arylsulfonyl group includes an arylsulfonyl group having a substituent and an unsubstituted arylsulfonyl group. Examples of the alkylsulfonyl group and arylsulfonyl group include a methylsulfonyl group and a phenylsulfonyl group.

The alkylsulfinyl group includes an alkylsulfinyl group having a substituent and an unsubstituted alkylsulfinyl group, and the arylsulfinyl group includes an arylsulfinyl group having a substituent and an unsubstituted arylsulfinyl group. Examples of the alkylsulfinyl group and arylsulfinyl group include a methylsulfinyl group and a phenylsulfinyl group.

The sulfamoyl group includes a sulfamoyl group having a substituent and an unsubstituted sulfamoyl group. Examples of the substituent include an alkyl group. Examples of the sulfamoyl group include a dimethylsulfamoyl group and a di-(2-hydroxyethyl)sulfamoyl group.

Next, the constituent group A_{11}, B_{11}, A, B and C of formulae (1), (3), (4), (6) and (7) are further described. In the following description about the constituent group A, B and C, those constituent group or substituent group has the same meanings as group of the same reference or the substituent group. As the above-described, the description of A_{11} and B_{11} is included in that of A and C, each being heterocyclic groups. Further, A in formula (3) is limited to a 5-membered

heterocyclic group.

In the following, those described above for each group or substituent also apply.

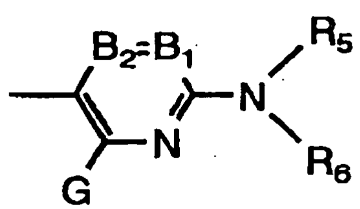
In each of formulae (1), (3), (4), (6) and (7), A, B and C each independently represents an aromatic group (A and C are a monovalent aromatic group such as aryl group, and B is a divalent aromatic group such as arylene group) which may be substituted, or a heterocyclic group (A and C are a monovalent heterocyclic group and B is a divalent heterocyclic group) which may be substituted. Examples of the aromatic ring include a benzene ring and a naphthalene ring. Examples of the heteroatom in the heterocyclic ring include N, O and S. The heterocyclic ring may be condensed with an aliphatic ring, an aromatic ring or another heterocyclic ring.

The substituent may be an arylazo group or a heterocyclic azo group.

A dye where at least two of A, B and C are a heterocyclic group is more preferred.

The heterocyclic group represented by C_{41} is preferably an aromatic nitrogen-containing 6-membered heterocyclic group represented by the following formula (8). When C is an aromatic nitrogen-containing 6-membered heterocyclic group represented by formula (8), formula (4) corresponds to formula (6).

Formula (6):



In formula (8), B_1 and B_2 each represents $=CR_1-$ or $-CR_2=$ or either one of B_1 and B_2 represents a nitrogen atom and the other represents $=CR_1-$ or $-CR_2=$. B_1 and B_2 each is preferably $=CR_1-$ or $-CR_2=$.

R_5 and R_6 each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, and each group may further have a substituent. The substituent represented by R_5 and R_6 is preferably a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group, and each group may further have a substituent. However, R_5 and R_6 are not a hydrogen atom at the same time.

G, R_1 and R_2 each independently represents a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a heterocyclic group, a cyano group, a carboxyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl group, an acyl group,

a hydroxy group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a silyloxy group, an acyloxy group, a carbamoyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, a heterocyclic sulfonylamino group, a nitro group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkylsulfonyl group, an arylsulfonyl group, a heterocyclic sulfonyl group, an alkylsulfinyl group, an arylsulfinyl group, a heterocyclic sulfinyl group, a sulfamoyl group or a sulfo group, and each group may be further substituted.

The substituent represented by G is preferably a hydrogen atom, a halogen atom, an aliphatic group, an aromatic group, a hydroxyl group, an alkoxy group, an aryloxy group, an acyloxy group, a heterocyclic oxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group), an acylamino group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylthio group, an arylthio group or a heterocyclic thio group, more preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxy group, an alkoxy group, an aryloxy group, an acyloxy group, an amino group (including an alkylamino group, an arylamino group and a heterocyclic amino group) or an acylamino group, and most preferably a hydrogen atom, an anilino group or an acylamino group, and each group may further have a substituent.

The substituents represented by R_1 and R_2 each is preferably a hydrogen atom, an alkyl group, a halogen atom, an alkoxycarbonyl group, a carboxyl group, a carbamoyl group, a hydroxy group, an alkoxy group or a cyano group, and each group may further have a substituent.

R_1 and R_5, or R_5 and R_6 may combine to form a 5- or 6-membered ring.

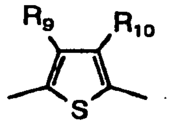
When the substituents represented by A, R_1, R_2, R_5, R_6 and G each further has a substituent, examples of the substituent include the substituents described above for G, R_1 and R_2. Also, an ionic hydrophilic group is preferably further present as a substituent on any one position of A, R_1, R_2, R_5, R_6 and G.

Examples of the ionic hydrophilic group as a substituent include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these, lithium ion is preferred.

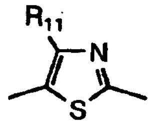
When B has a ring structure, preferred examples of the heterocyclic ring include a thiophene

ring, a thiazole ring, an imidazole ring, a benzothiazole ring and a thienothiazole ring. Each heterocyclic group may further have a substituent. Among these heterocyclic rings, a thiophene ring, a thiazole ring, an imidazole ring, a benzothiazole ring and a thienothiazole ring represented by the following formulae (a) to (e) are preferred. When B is a thiophene ring represented by formula (a) and C_{41} is a structure represented by formula (8), formula (6) corresponds to formula (7).

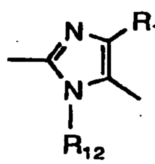
(a)



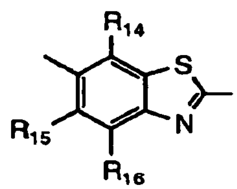
(b)



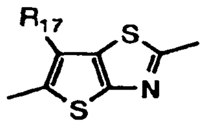
(c)



(d)



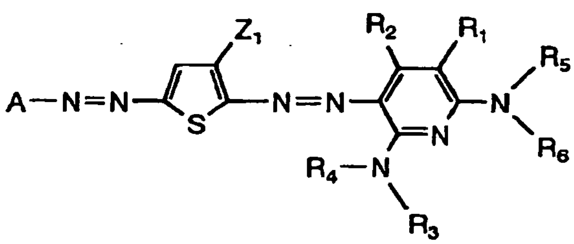
(e)



In formula (a) to (e), R_9 to R_{17} each represents a substituent having the same meaning as G, R_1 and R_2 in formula (6).

Particularly preferred is a structure represented by the following formula (9):

Formula (9):



In formula (9), Z_1 represents an electron-withdrawing group having a Hammett's substituent constant σp value of 0.20 or more. Z_1 is preferably an electron-withdrawing group having a σp value of 0.30 or more, more preferably 0.45 or more, still more preferably 0.60 to more, but the σp value preferably does not exceed 1.0. Among these, Z_1 is preferably an acyl group having from 2 to 20 carbon atoms, an alkyloxycarbonyl group having from 2 to 20 carbon atoms, a nitro group, a cyano group, an alkylsulfonyl group having from 1 to 20 carbon atoms, an arylsulfonyl group having from 6 to 20 carbon atoms, a carbamoyl group having from 1 to 20 carbon atoms or a halogenated alkyl group having from 1 to 20 carbon atoms, more preferably a cyano group, an alkylsulfonyl group

having from 1 to 20 carbon atoms and an arylsulfonyl group having from 6 to 20 carbon atoms, and most preferably a cyano group.

R_1, R_2, R_5 and R_6 have the same meanings as in formula (6). R_3 and R_4 each independently represents a hydrogen atom, an aliphatic group, an aromatic group, a heterocyclic group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group or a sulfamoyl group, preferably a hydrogen atom, an aromatic group, a heterocyclic group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group, more preferably a hydrogen atom, an aromatic group or a heterocyclic group.

The groups described in regard to formula (9) each may further have a substituent. When these groups each further has a substituent, examples of the substituent include the substituents described in regard to formula (6), the groups described as examples for G, R_1 and R_4
$_2$, and ionic hydrophilic groups.

The Hammett's substituent constant σp value is briefly described here. The Hammett's rule is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a σp value and a σm value and these values can be found in a large number of general publications but these are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979). In the present invention, each substituent is limited or described by using the Hammett's substituent constant σp but this does not mean that the substituent is limited only to those having a known value which can be found in the above-described publications. Needless to say, the substituent includes substituents of which σp value is not known in publications but when measured based on the Hammett's rule, falls within the range specified. Furthermore, although the dye of formula (1), (3), (4), (6), (7) or (9) of the present invention includes those which are not a benzene derivative, the σp value is used as a measure for showing the electron effect of the substituent irrespective of the substitution site. In the present invention, the σp value is used in this meaning.

Specific examples of the electron-withdrawing group having a Hammett's substituent constant σp value of 0.60 or more include a cyano group, a nitro group, an alkylsulfonyl group (e.g., methanesulfonyl) and an arylsulfonyl group (e.g., benzenesulfonyl).

Specific examples of the electron-withdrawing group having a Hammett's σp value of 0.45 or more include, in addition to those described above, an acyl group (e.g., acetyl), an alkoxycarbonyl group (e.g., dodecyloxycarbonyl), an aryloxycarbonyl group (e.g., m-chlorophenoxycarbonyl), an alkylsulfinyl group (e.g., n-propylsulfinyl), an arylsulfinyl group (e.g., phenylsulfinyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dimethylsulfamoyl) and a halogenated alkyl group (e.g., trifluoromethyl).

Specific examples of the electron-withdrawing group having a Hammett's substituent constant σp value of 0.30 or more include, in addition to those described above, an acyloxy group (e.g., acetoxy), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a halogenated alkoxy group (e.g., trifluoromethyloxy), a halogenated aryloxy group (e.g., pentafluorophenyloxy), a sulfonyloxy group (e.g., methylsulfonyloxy), a halogenated alkylthio group (e.g., difluoromethylthio), an aryl group substituted by two or more electron-withdrawing groups having a σp value of 0.15 or more (e.g., 2,4-dinitrophenyl, pentachlorophenyl) and a heterocyclic ring (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl).

Specific examples of the electron-withdrawing group having a σp value of 0.20 or more include, in addition to those described above, a halogen atom.

The preferred combination of substituents in the azo dye represented by formula (1), (3), (4) or (6) is described below. R_5 and R_6 each is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, a sulfonyl group or an acyl group, more preferably a hydrogen atom, an aryl group, a heterocyclic group or a sulfonyl group, and most preferably a hydrogen atom, an aryl group or a heterocyclic group. However, R_5 and R_6 are not a hydrogen atom at the same time.

G is preferably a hydrogen atom, a halogen atom, an alkyl group, a hydroxyl group, an amino group or an acylamino group, more preferably a hydrogen atom, a halogen atom, an amino group or an acylamino group, and most preferably a hydrogen atom, an amino group or an acylamino group.

A is preferably a pyrazole ring, an imidazole ring, an isothiazole ring, a thiadiazole ring or a benzothiazole ring, more preferably a pyrazole ring or an isothiazole ring, and most preferably a pyrazole ring.

B_1 and B_2 each is $=CR_1-$ or $-CR_2=$, and R_1 and R_2 each is preferably a hydrogen atom, an alkyl group, a halogen atom, a cyano group, a carbamoyl group, a carboxyl group, a hydroxyl group, an alkoxy group or an alkoxycarbonyl group, more preferably a hydrogen atom, an alkyl group, a carboxyl group, a cyano group or a carbamoyl group.

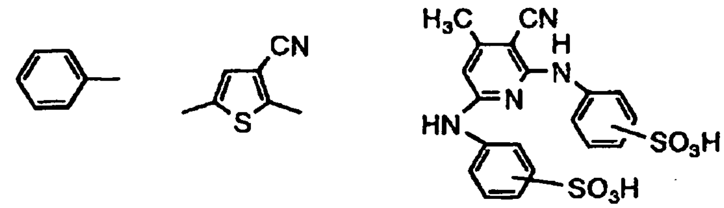
As for the preferred combination of substituents in the azo dye of formula (1), (3), (4), (6) or (7), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

Specific examples of the azo dye represented by formula (1), (3), (4), (6) or (7) are set forth below, however, the present invention is not limited to those set forth below. In these specific examples, the carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these, lithium ion is preferred.

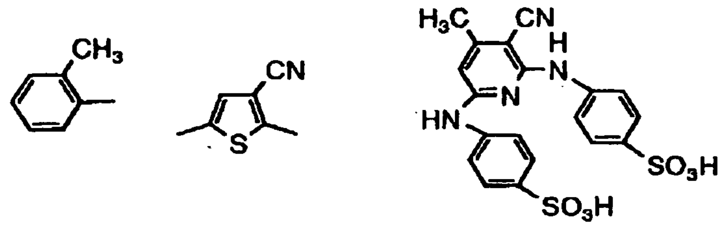
$$A-N=N-B-N=N-C$$

A B C

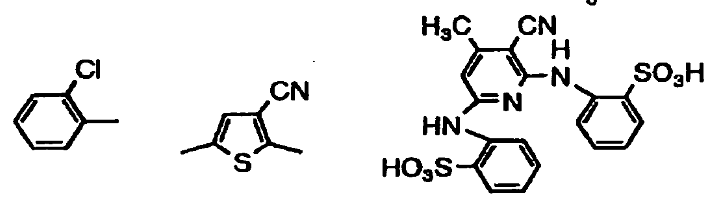
(a-1)



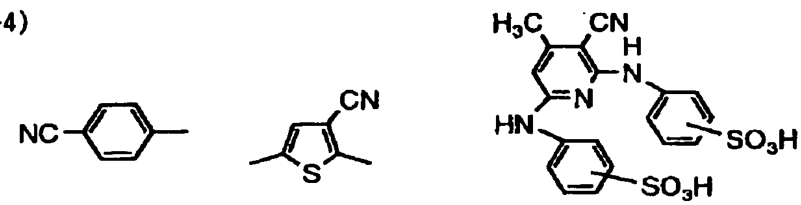
(a-2)



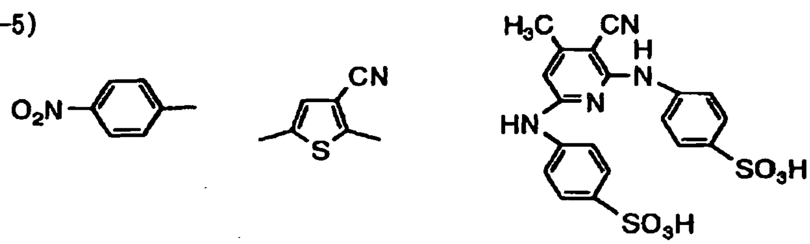
(a-3)



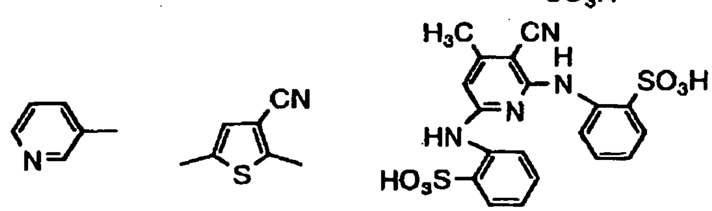
(a-4)



(a-5)



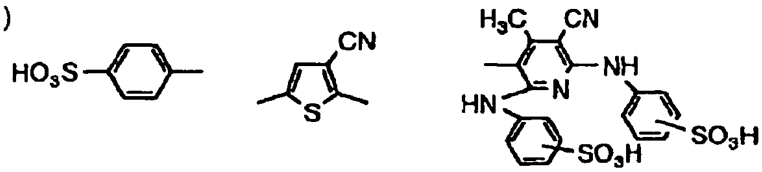
(a-6)



A—N=N—B—N=N—C

A	B	C

(b-1)



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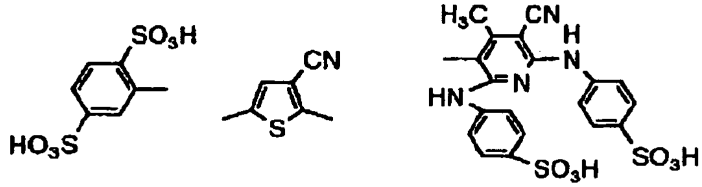
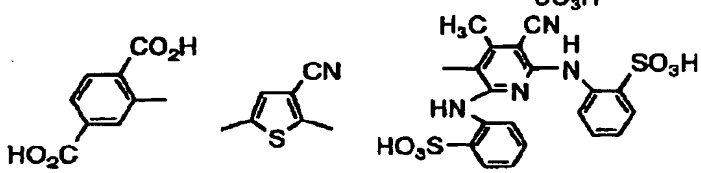
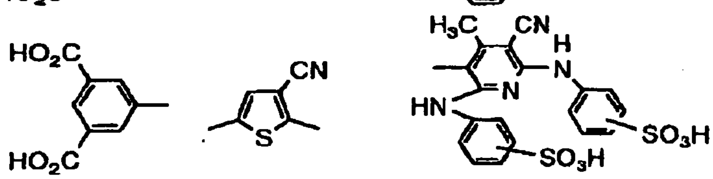


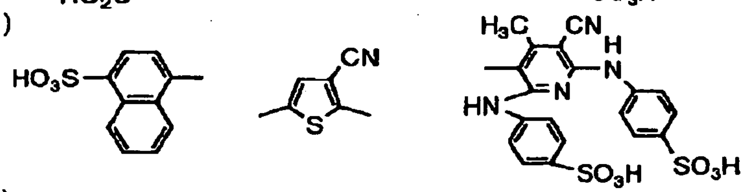
(b-3)



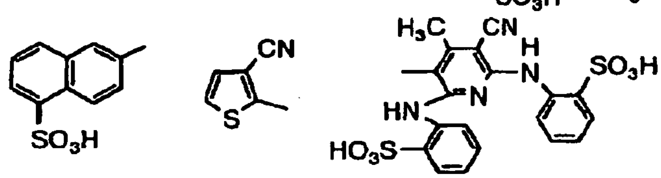
(b-4)



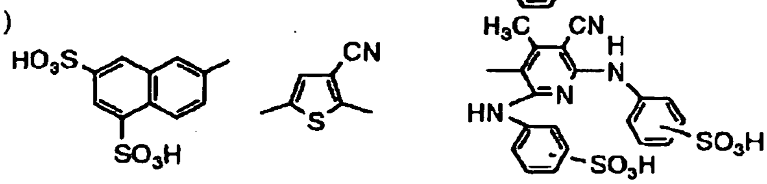
(b-5)



(b-6)



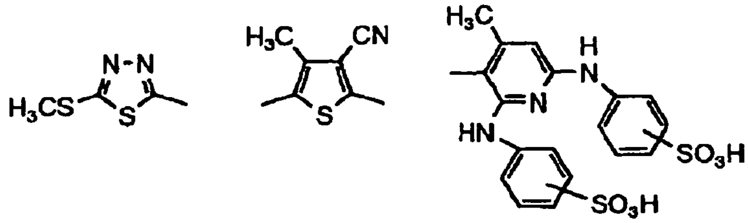
(b-7)



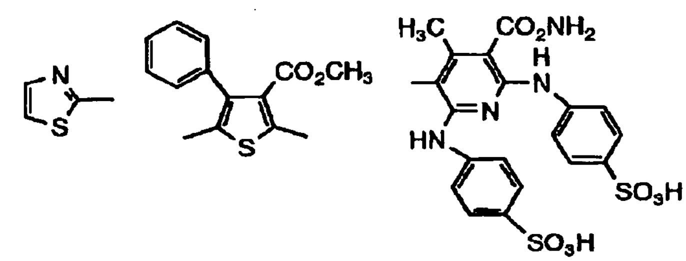
$$A—N=N—B—N=N—C$$

A B C

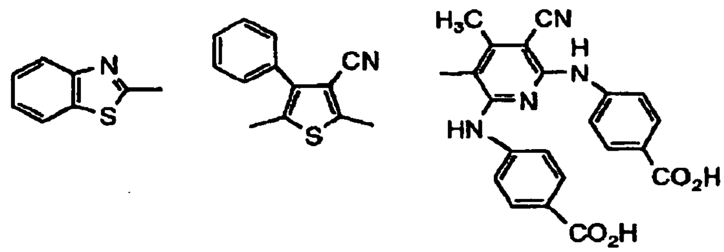
(c-1)



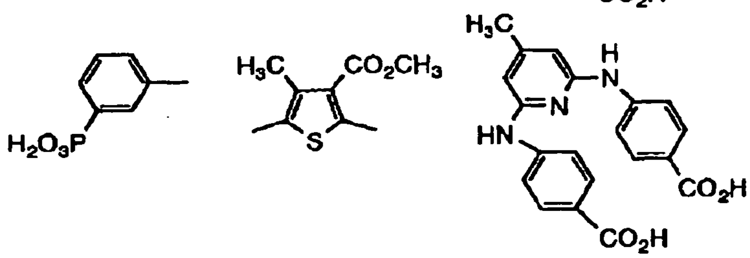
(c-2)



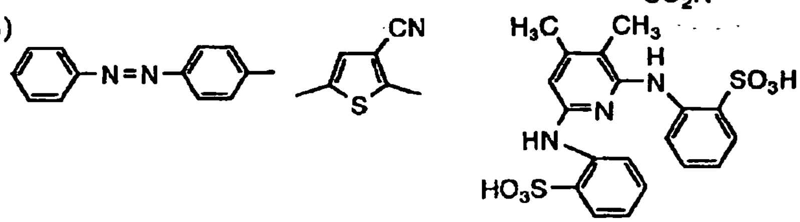
(c-3)



(c-4)



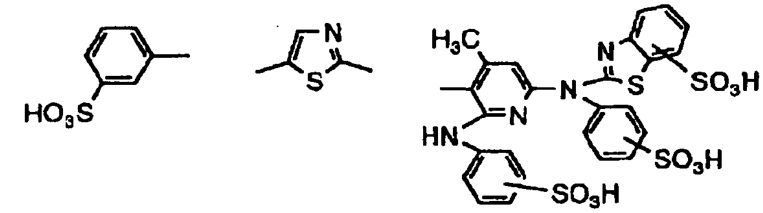
(c-5)



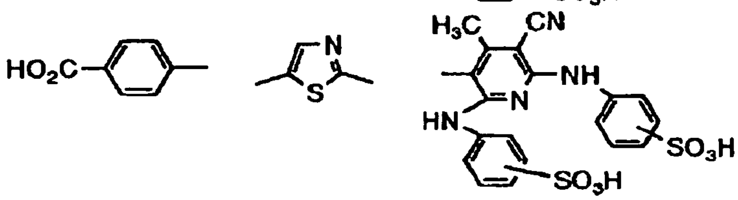
A—N=N—B—N=N—C

A B C

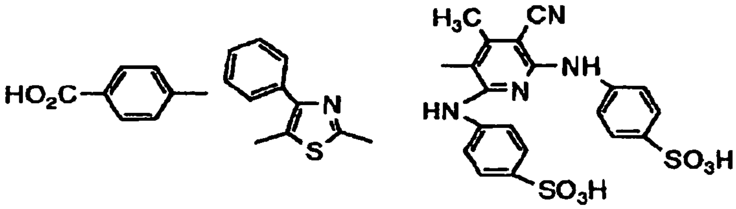
(d-1)



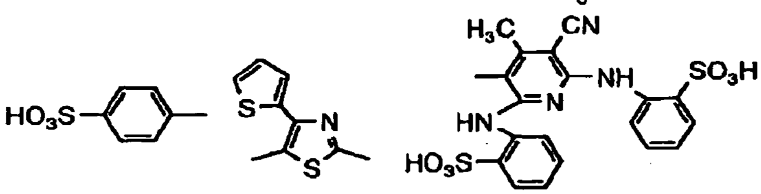
(d-2)



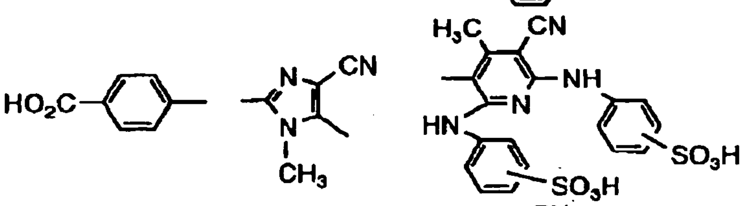
(d-3)



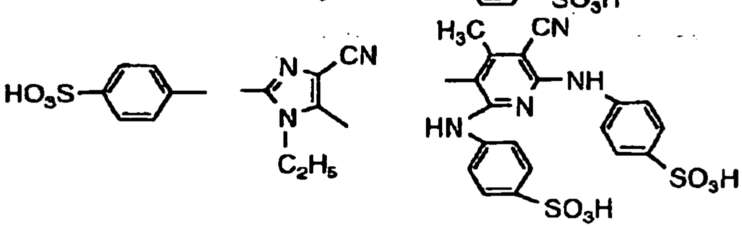
(d-4)



(d-5)



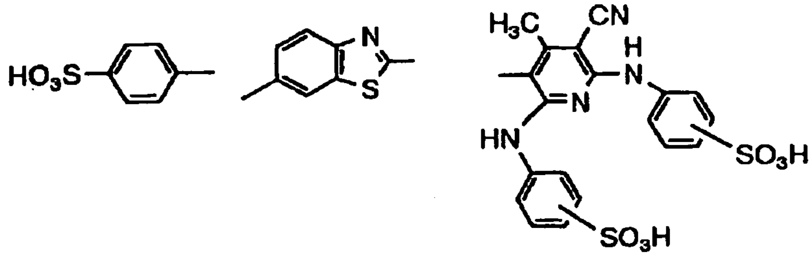
(d-6)



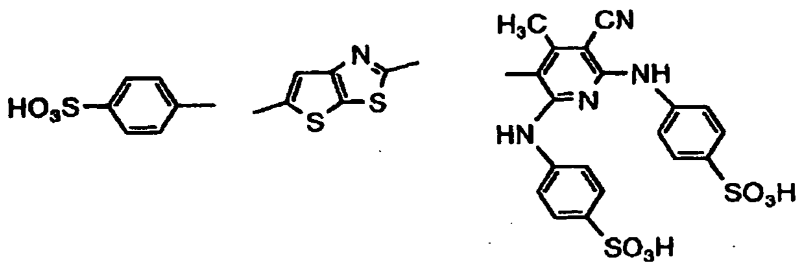
$$A-N{=}N-B-N{=}N-C$$

A B C

(e-1)



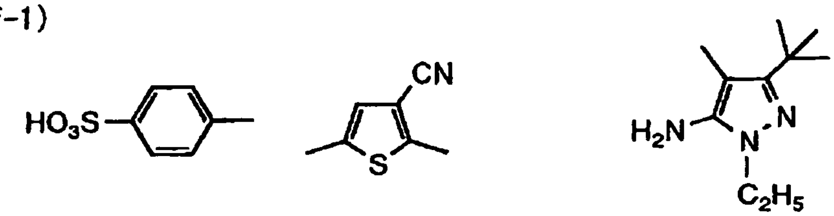
(e-2)



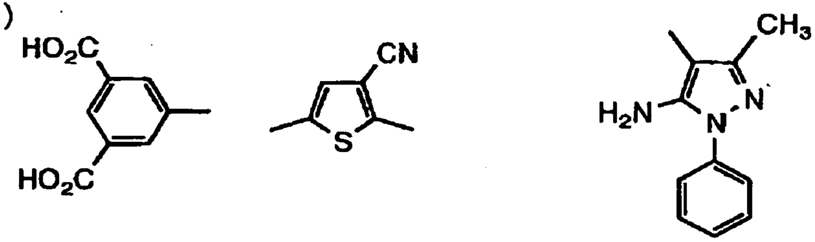
A—N=N—B—N=N—C

A B C

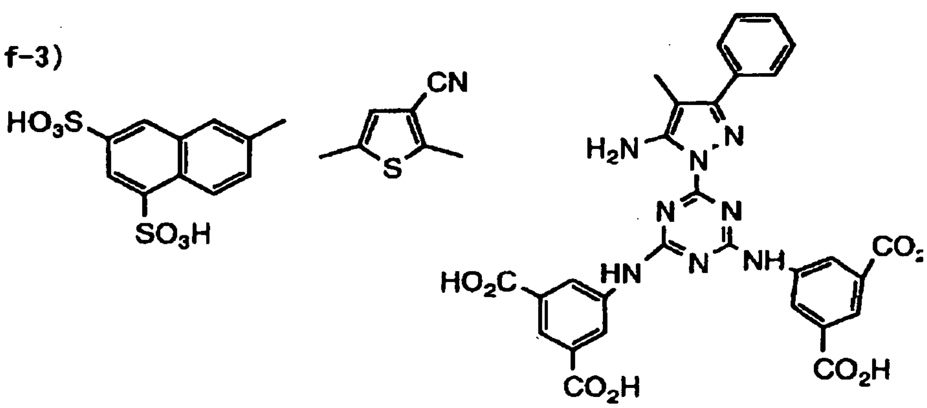
(f-1)



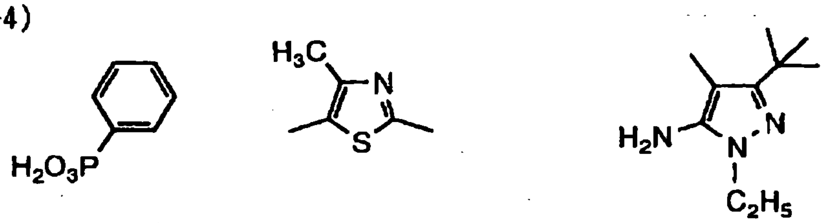
(f-2)



(f-3)



(f-4)

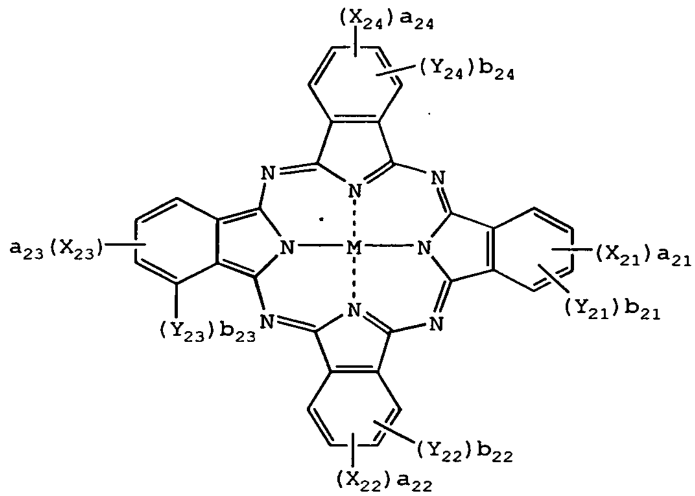


The azo dyes represented by formulae (1), (3), (4), (6) and (7) can be synthesized by a coupling reaction of a diazo component and a coupler. As the main synthesis method, the method described in JP2002-113460 can be used.

As the longer wavelength-absorbing dye, the dye represented by formula (2) is preferably used with the dye of formula (1), (3), (4), (6) or (7).

Next, the dye of formula (2) is described in detail below.

Formula (2):



In formula (2), X_{21}, X_{22}, X_{23} and X_{24} each independently represents -SO-Z, -SO_2-Z, -$SO_2NR_{21}R_{22}$, a sulfo group, -$CONR_{21}R_{22}$ or -$COOR_{21}$,

each Z independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group,

R_{21} and R_{22} each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group,

Y_{21}, Y_{22}, Y_{23} and Y_{24} each independently represents a monovalent substituent,

a_{21} to a_{24} and b_{21} to b_{24} represent the number of substituents X_{21} to X_{24} and Y_{21} to Y_{24}, respectively, a_{21} to a_{24} each independently represents a number of 0 to 4 but all are not 0 at the same time, and b_{21} to b_{24} each independently represents a number of 0 to 4, provided that when a_{21} to a_{24} and b_{21} to b_{24} each represents a number of 2 or more, the plurality of X_{21}s, X_{22}s, X_{33}s, X_{24}s, Y_{21}s, Y_{22}s, Y_{23}s or Y_{24}s may be the same or different, and

M represents a hydrogen atom, a metal atom or an oxide, hydroxide or halide thereof.

The compound represented by formula (2) is described in detail below.

In formula (2), X_{21}, X_{22}, X_{23} and X_{24} each independently represents -SO-Z, -SO_2-Z, -$SO_2NR_{21}R_{22}$, a sulfo group, -$CONR_{21}R_{22}$ or -CO_2R_{21}. Among these substituents, preferred are -SO-Z, -SO_2-Z, -$SO_2NR_{21}R_{22}$ and -$CONR_{21}R_{22}$, more preferred are -SO_2-Z and -$SO_2NR_{21}R_{22}$, and most preferred is -SO_2-Z. In the case where a_{21} to a_{24} each showing the number of substituents each represents a number of 2 or more, the plurality of X_{21}s, X_{22}s, X_{23}s or X_{24}s may be the same or different and each independently represents any one of the above-described groups. X_{21}, X_{22}, X_{23}

and X_{24} may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where X_{21}, X_{22}, X_{23} and X_{24} all are $-SO_2-Z$ and Zs are different from each other, or may include substituents different from each other (for example, $-SO_2-Z$ and $-SO_2NR_{21}R_{22}$).

Each Z independently represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group.

R_{21} and R_{22} each independently represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, more preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that R_{21} and R_{22} both are a hydrogen atom.

The substituted or unsubstituted alkyl group represented by R_{21}, R_{22} and Z is preferably an alkyl group having from 1 to 30 carbon atoms, more preferably a branched alkyl group because the solubility of dye and the stability of ink are improved, and still more preferably an alkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the alkyl group may be substituted by a halogen atom or an ionic hydrophilic group. Incidentally, the number of carbon atoms in the alkyl group does not contain carbon atoms of substituents and this applies to other groups.

The substituted or unsubstituted cycloalkyl group represented by R_{21}, R_{22} and Z is preferably a cycloalkyl group having from 5 to 30 carbon atoms, more preferably a cycloalkyl group having an asymmetric carbon (use in the racemic form) because the solubility of dye and the stability of ink are improved. Examples of the substituent include those described later as the substituent when Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the cycloalkyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted alkenyl group represented by R_{21}, R_{22} and Z is preferably an alkenyl group having from 2 to 30 carbon atoms, more preferably a branched alkenyl group because the solubility of dye and the stability of ink are improved, and still more preferably an alkenyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the alkenyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted aralkyl group represented by R_{21}, R_{22} and Z is preferably an aralkyl group having from 7 to 30 carbon atoms, more preferably a branched aralkyl group because the solubility of dye and the stability of ink are improved, and still more preferably an aralkyl group having an asymmetric carbon (use in the racemic form). Examples of the substituent include those described later as the substituent when Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} can further have a substituent. In particular, a hydroxyl group, an ether group, an ester group, a cyano group, an amido group and a sulfonamido group are preferred because the aggregating property and fastness of dye are enhanced. Other than these, the aralkyl group may be substituted by a halogen atom or an ionic hydrophilic group.

The substituted or unsubstituted aryl group represented by R_{21}, R_{22} and Z is preferably an aryl group having from 6 to 30 carbon atoms. Examples of the substituent include those described later as the substituent when Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} can further have a substituent. In particular, an electron-withdrawing group is preferred because the dye can have a noble oxidation potential and be improved in the fastness. Examples of the electron-withdrawing group include those having a positive Hammett's substituent constant σp value. Among these, preferred are a halogen atom, a heterocyclic group, a cyano group, a carboxyl group, an acylamino group, a sulfonamido group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group, more preferred are a cyano group, a carboxyl group, a sulfamoyl group, a carbamoyl group, a sulfonyl group, an imido group, an acyl group, a sulfo group and a quaternary ammonium group.

The heterocyclic group represented by R_{21}, R_{22} and Z is preferably a 5- or 6-membered ring and the ring may be further condensed. Also, the ring may be an aromatic heterocyclic ring or a non-aromatic heterocyclic ring. Examples of the heterocyclic group represented by R_{21}, R_{22} and Z_2 are shown below in the form of a heterocyclic ring by omitting the substitution site. The substitution site is not limited and, for example, in the case of pyridine, the 2-position, 3-position and 4-position can be substituted. Examples include pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, pyrrole, indole, furan, benzofuran,

thiophene, benzothiophene, pyrazole, imidazole, benzimidazole, triazole, oxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, thiadiazole, isoxazole, benzisoxazole, pyrrolidine, piperidine, piperazine, imidazolidine and thiazoline. In particular, an aromatic heterocyclic group is preferred. Preferred examples thereof include, shown in the same manner as above, pyridine, pyrazine, pyrimidine, pyridazine, triazine, pyrazole, imidazole, benzimidazole, triazole, thiazole, benzothiazole, isothiazole, benzisothiazole and thiadiazole. These groups each may have a substituent and examples of the substituent include those described later as the substituent when Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} can further have a substituent. Preferred substituents are the same as the above-described substituents of the aryl group and more preferred substituents are the same as the above-described more preferred substituents of the aryl group.

Y_{21}, Y_{22}, Y_{23} and Y_{24} each independently represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, an amino group, an alkylamino group, an alkoxy group, an aryloxy group, an acylamino group, an arylamino group, a ureido group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonyl group, an aryloxycarbonylamino group, an imido group, a heterocyclic thio group, a phosphoryl group, an acyl group, a carboxyl group or a sulfo group. These groups each may further have a substituent.

Y_{21}, Y_{22}, Y_{23} and Y_{24} each is preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

When Z, R_{21}, R_{22}, Y_{21}, Y_{22}, Y_{23} and Y_{24} each is a group which can further have a substituent, the group may further have the following substituent.

Examples of the substituent include a linear or branched alkyl group having from 1 to 12 carbon atoms, a linear or branched aralkyl group having from 7 to 18 carbon atoms, a linear or branched alkenyl group having from 2 to 12 carbon atoms, a linear or branched alkynyl group having from 2 to 12 carbon atoms, a linear or branched cycloalkyl group having from 3 to 12 carbon atoms, a linear or branched cycloalkenyl group having from 3 to 12 carbon atoms (these groups each is preferably a group having a branched chain because the solubility of dye and the stability of ink are improved, more preferably a group having an asymmetric carbon; specific examples of the groups include a methyl group, an ethyl group, a propyl group, an isopropyl group, a sec-butyl group, a tert-butyl group, a 2-ethylhexyl group, a 2-methylsulfonylethyl group, a 3-phenoxypropyl group, a

trifluoromethyl group and a cyclopentyl group), a halogen atom (e.g., chlorine, bromine), an aryl group (e.g., phenyl, 4-tert-butylphenyl, 2,4-di-tert-amylphenyl), a heterocyclic group (e.g., imidazolyl, pyrazolyl, triazolyl, 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl), a cyano group, a hydroxyl group, a nitro group, a carboxy group, an amino group, an alkyloxy group (e.g., methoxy, ethoxy, 2-methoxyethoxy, 2-methanesulfonylethoxy), an aryloxy group (e.g., phenoxy, 2-methylphenoxy, 4-tert-butylphenoxy, 3-nitrophenoxy, 3-tert-butyloxycarbamoylphenoxy, 3-methoxycarbamoyl), an acylamino group (e.g., acetamido, benzamido, 4-(3-tert-butyl-4-hydroxyphenoxy)butanamido), an alkylamino group (e.g., methylamino, butylamino, diethylamino, methylbutylamino), an anilino group (e.g., phenylamino, 2-chloroanilino), a ureido group (e.g., phenylureido, methylureido, N,N-dibutylureido), a sulfamoylamino group (e.g., N,N-dipropylsulfamoylamino), an alkylthio group (e.g., methylthio, octylthio, 2-phenoxyethylthio), an arylthio group (e.g., phenylthio, 2-butoxy-5-tert-octylphenylthio, 2-carboxyphenylthio), an alkyloxycarbonylamino group (e.g., methoxycarbonylamino), a sulfonamido group (e.g., methanesulfonamido, benzenesulfonamido, p-toluenesulfonamido), a carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl), a sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-phenylsulfamoyl), a sulfonyl group (e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl, toluenesulfonyl), an alkyloxycarbonyl group (e.g., methoxycarbonyl, butyloxycarbonyl), a heterocyclic oxy group (e.g., 1-phenyltetrazol-5-oxy, 2-tetrahydropyranyloxy), an azo group (e.g., phenylazo, 4-methoxyphenylazo, 4-pivaloylaminophenylazo, 2-hydroxy-4-propanoylphenylazo), an acyloxy group (e.g., acetoxy), a carbamoyloxy group (e.g., N-methylcarbamoyloxy, N-phenylcarbamoyloxy), a silyloxy group (e.g., trimethylsilyloxy, dibutylmethylsilyloxy), an aryloxycarbonylamino group (e.g., phenoxycarbonylamino), an imido group (e.g., N-succinimido, N-phthalimido), a heterocyclic thio group (e.g., 2-benzothiazolylthio, 2,4-di-phenoxy-1,3,5-triazole-6-thio, 2-pyridylthio), a sulfinyl group (e.g., 3-phenoxypropylsulfinyl), a phosphonyl group (e.g., phenoxyphosphonyl, octyloxy-phosphonyl, phenylphosphonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), an acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl), and an ionic hydrophilic group (e.g., carboxyl, sulfo, phosphono, quaternary ammonium).

In the case where the phthalocyanine dye represented by formula (2) is water-soluble, the dye preferably contains an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, alkali metal salts are preferred and a lithium salt is more preferred because

the solubility of dye and the stability of ink are improved.

As for the number of ionic hydrophilic groups, the phthalocyanine dye preferably contains at least two ionic hydrophilic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule.

In formula (2), a_{21} to a_{24} and b_{21} to b_{24} represent the number of substituents X_{21} to X_{24} and Y_{21} to Y_{24}, respectively. a_{21} to a_{24} each independently represents an integer of 0 to 4 but all are not 0 at the same time. b_{21} to b_{24} each independently represents an integer of 0 to 4. When a_{21} to a_{24} and b_{21} to b_{24} each represents an integer of 2 or more, a plurality of substituents X_{21}, X_{22}, X_{23}, X_{24}, Y_{21}, Y_{22}, Y_{23} or Y_{24} may be the same or different.

a_{21} and b_{21} satisfy the relationship of $a_{21}+b_{21}=4$. In particular, a combination that a_{21} represents 1 or 2 and b_{21} represents 3 or 2 is preferred, and a combination that a_{21} represents 1 and b_{21} represents 3 is most preferred.

The same relationship as that between a_{21} and b_{21} is present in each of the pairs a_{22} and b_{22}, a_{23} and b_{23}, and a_{24} and b_{24}, and the preferred combination is also the same.

M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof.

M is preferably a hydrogen atom, a metal element such as Li, Na, K, Mg, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Si, Ge, Sn, Pb, Sb and Bi, an oxide such as VO and GeO, a hydroxide such as $Si(OH)_2$, $Cr(OH)_2$ and $Sn(OH)_2$, or a halide such as AlCl, $SiCl_2$, VCl, VCl_2, VOCl, FeCl, GaCl and ZrCl.

Among these, more preferred are Cu, Ni, Zn and Al, and most preferred is Cu.

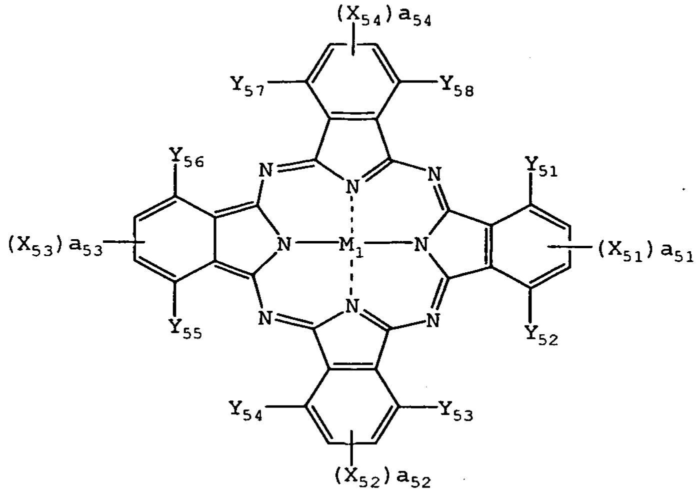
In the phthalocyanine dye represented by formula (2), Pc (phthalocyanine ring) may also form a dimer (for example, Pc-M-L-M-Pc) or a trimer through L (divalent linking group). At this time, Ms may be the same or different.

The divalent linking group represented by L is preferably an oxy group -O-, a thio group -S-, a carbonyl group -CO-, a sulfonyl group $-SO_2-$, an imino group -NH-, a methylene group $-CH_2-$ or a group formed by combining two or more of these groups.

As for the preferred combination of substituents in the compound represented by formula (2), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

Among the phthalocyanine dyes represented by formula (2), preferred is a phthalocyanine dye having a structure represented by the following formula (5):

Formula (5):



In formula (5), X_{51} to X_{54} and Y_{51} to Y_{58} have the same meanings as X_{21} to X_{24} and Y_{21} to Y_{24} in formula (2), respectively, and preferred examples are also the same. M has the same meaning as M in formula (2) and preferred examples are also the same.

In formula (5), a_{51} to a_{54} each independently represents an integer of 1 or 2 and preferably satisfy $4 \leq a_{51}+a_{52}+a_{53}+a_{54} \leq 6$, and $a_{51}=a_{52}=a_{53}=a_{54}=1$ is more preferred.

X_{51}, X_{52}, X_{53} and X_{54} may be completely the same substituents, may be substituents of the same kind but partially different as in the case, for example, where X_{51}, X_{52}, X_{53} and X_{54} all are $-SO_2$-Z and Zs are different from each other, or may include substituents different from each other, for example, $-SO_2$-Z and $-SO_2NR_{21}R_{22}$.

In the phthalocyanine dye represented by formula (5), the following combinations of substituents are particularly preferred.

X_{51} to X_{54} each independently represents preferably -SO-Z, $-SO_2$-Z, $-SO_2NR_{21}R_{22}$ or $-CONR_{21}R_{22}$, more preferably $-SO_2$-Z or $-SO_2NR_{21}R_{22}$, and most preferably $-SO_2$-Z.

Z is preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, and most preferably a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregating property and fastness are improved.

R_{21} and R_{22} each independently represents preferably a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocyclic group, more preferably a hydrogen atom, a substituted alkyl group, a substituted aryl group or a substituted heterocyclic group. However, it is not preferred that R_{21} and R_{22} both are a

hydrogen atom. In particular, the case where an asymmetric carbon is present in the substituent (use in the racemic form) is preferred because the solubility of dye and the stability of ink are enhanced. Also, the case where a hydroxyl group, an ether group, an ester group, a cyano group, an amido group or a sulfonamido group is present in the substituent is preferred because the aggregating property and fastness are improved.

Y_{51} to Y_{58} each independently represents preferably a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a cyano group, an alkoxy group, an amido group, a ureido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group, a carboxyl group or a sulfo group, more preferably a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or a sulfo group, and most preferably a hydrogen atom.

a_{51} to a_{54} each independently represents preferably 1 or 2 and it is more preferred that all are 1.

M represents a hydrogen atom, a metal element or an oxide, hydroxide or halide thereof, more preferably Cu, Ni, Zn or Al, and most preferably Cu.

In the case where the phthalocyanine dye represented by formula (5) is water-soluble, the dye preferably contains an ionic hydrophilic group. Examples of the ionic hydrophilic group include a sulfo group, a carboxyl group, a phosphono group and a quaternary ammonium group. Among these ionic hydrophilic groups, preferred are a carboxyl group, a phosphono group and a sulfo group, more preferred are a carboxyl group and a sulfo group. The carboxyl group, the phosphono group and the sulfo group each may be in a salt state and examples of the counter ion for forming the salt include ammonium ion, alkali metal ions (e.g., lithium ion, sodium ion, potassium ion) and organic cations (e.g., tetramethylammonium ion, tetramethylguanidium ion, tetramethylphosphonium). Among these counter ions, alkali metal salts are preferred and a lithium salt is more preferred because the solubility of dye and the stability of ink are improved.

As for the number of ionic hydrophilic groups, the phthalocyanine-base dye preferably contains at least two ionic hydrophilic groups, more preferably at least two sulfo groups and/or carboxyl groups, within one molecule.

As for the preferred combination of substituents in the compound represented by formula (5), a compound where at least one of various substituents is the preferred group is preferred, a compound where a larger number of various substituents are the preferred groups is more preferred, and a compound where all substituents are the preferred groups is most preferred.

As for the chemical structure of the phthalocyanine dye represented by formula (5), at least one electron-withdrawing group such as sulfinyl group, sulfonyl group and sulfamoyl group is preferably introduced into respective four benzene rings of phthalocyanine such that the total of σp values of the substituents in the entire phthalocyanine skeleton becomes 1.6 or more.

The Hammett's substituent constant σp value is briefly described here. The Hammett's rule

is an empirical rule advocated by L.P. Hammett in 1935 so as to quantitatively discuss the effect of substituent on the reaction or equilibrium of benzene derivatives and its propriety is widely admitted at present. The substituent constant determined by the Hammett's rule includes a σp value and a σm value and these values can be found in a large number of general publications but these are described in detail, for example, in J.A. Dean (compiler), Lange's Handbook of Chemistry, 12th ed., McGraw-Hill (1979), and Kagakuno Ryoiki (Chemistry Region), special number, No. 122, pp. 96-103, Nankodo (1979). In the present invention, each substituent is limited or described by using the Hammett's substituent constant σp but this does not mean that the substituent is limited only to those having a known value which can be found in the above-described publications. Needless to say, the substituent includes substituents of which σp value is not known in publications but when measured based on the Hammett's rule, falls within the range specified. Furthermore, although the dye for use in the present invention includes those which are not a benzene derivative, the σp value is used as a measure for showing the electron effect of the substituent irrespective of the substitution site. In the present invention, the σp value is used in this meaning.

Inevitably in view of the synthesis method, the phthalocyanine dye represented by formula (2) is generally a mixture of analogues differing in the site where the substituents Xn (n=1 to 4) and Ym (m=1 to 4) are introduced and in the number of the substituents introduced. Accordingly, these analogue mixtures are statistically averaged and represented by a formula in many cases. In the present invention, it has been found that when these analogue mixtures are classified into the following three types, a specific mixture is particularly preferred. The phthalocyanine-base dye analogue mixtures represented by formulae (2) and (5) are defined by classifying these into the following three types based on the substitution site. The positions of Y_{51}, Y_{52}, Y_{53}, Y_{54}, Y_{55}, Y_{56}, Y_{57} and Y_{58} in formula (5) are designated as 1, 4, 5, 8, 9, 12, 13 and 16, respectively.

(1) β-Position substitution type:

A phthalocyanine dye having specific substituents at the 2- and/or 3-position, the 6- and/or 7-position, the 10- and/or 11-position, and the 14- and/or 15-position.

(2) α-Position substitution type:

A phthalocyanine dye having specific substituents at the 1- and/or 4-position, the 5- and/or 8-position, the 9- and/or 12-position, and the 13- and/or 16-position.

(3) α,β-Position mixed substitution type:

A phthalocyanine dye having specific substitutions at the 1- to 16-positions without any regularity.

In the present invention, phthalocyanine dye derivatives differing in the structure (particularly in the substitution site) are described by using these β-position substitution type, α-position substitution type and α,β-position mixed substitution type.

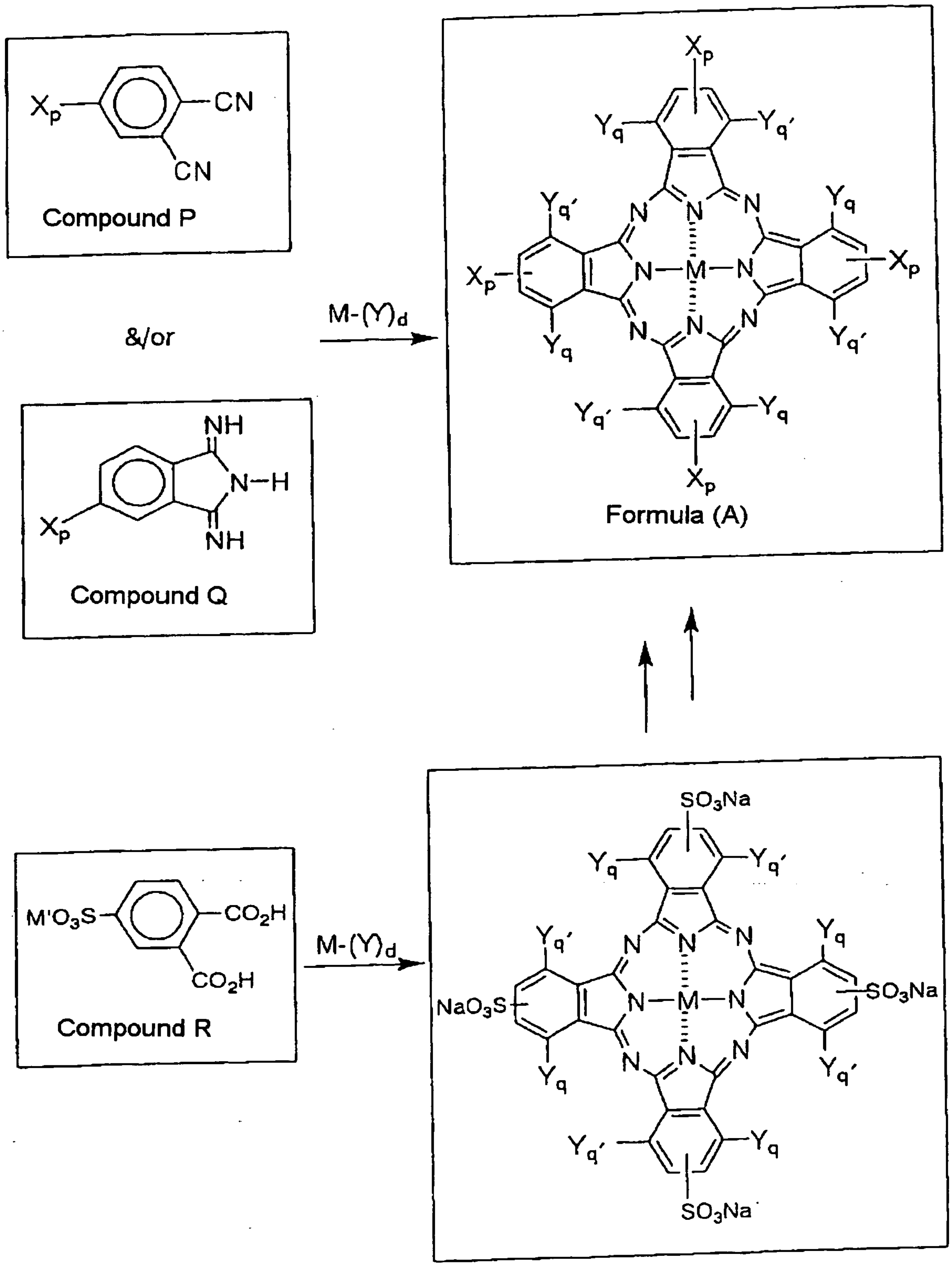
The phthalocyanine derivative for use in the present invention can be synthesized by

combining the methods described or cited, for example, in Shirai and Kobayashi, Phthalocyanine - Kagaku to Kino- (Phthalocyanine -Chemistry and Function-), pp. 1-62, IPC, and C.C. Leznoff and A.B.P. Lever, Phthalocyanines - Properties and Applications, pp. 1-54, VCH, or methods analogous thereto.

The phthalocyanine dye represented by formula (2) of the present invention can be synthesized, for example, through sulfonation, sulfonyl chloridation or amidation of an unsubstituted phthalocyanine compound as described in International Publications 00/17275, 00/08103, 00/08101 and 98/41853 and JP-A-10-36471. In this case, sulfonation may take place at any site of the phthalocyanine nucleus and the number of sites sulfonated is difficult to control. Accordingly, when a sulfo group is introduced under such reaction conditions, the positions and number of sulfo groups introduced into the product cannot be specified and a mixture of those differing in the number of substituents or in the substitution site inevitably results. If the dye is synthesized starting from such a product, the phthalocyanine dye is obtained as an α,β-position mixed substitution type mixture containing several kinds of compounds differing in the number of substituents or in the substitution site because the number of sulfamoyl groups substituted on the heterocyclic ring or their substitution sites cannot be specified.

As described above, for example, when many electron-withdrawing groups such as sulfamoyl group are introduced into the phthalocyanine nucleus, the oxidation potential becomes nobler and the ozone resistance is increased. However, according to the above-described synthesis method, a phthalocyanine dye where the number of electron-withdrawing groups introduced is small, namely, the oxidation potential is baser, is inevitably mingled. Therefore, in order to improve the ozone resistance, it is preferred to use a synthesis method where the production of a compound having a baser oxidation potential is suppressed.

The phthalocyanine compound represented by formula (2) or (5) for use in the present invention can be synthesized, for example, by reacting a phthalonitrile derivative (Compound P) shown below and/or a diiminoisoindoline derivative (Compound Q) shown below with a metal derivative represented by formula (III) or can be derived from a tetrasulfophthalocyanine compound obtained by reacting a 4-sulfophthalonitrile derivative (Compound R) shown below with a metal derivative represented by formula (III). (In the following chemical reaction scheme, the phthalocyanine compound represented by formula (2) or (5) is represented by formual (A).)



In the formulae above, X_p corresponds to X_{51}, X_{52}, X_{53} or X_{54} in formula (5) and Y_q and $Y_{q'}$ each corresponds to Y_{51}, Y_{52}, Y_{53}, Y_{54}, Y_{55}, Y_{56}, Y_{57} or Y_{58} in formula (5). In Compound R, M'

represents cation.

Examples of the cation represented by M' include alkali metal ions such as Li, Na and K, and organic cations such as triethylammonium ion and pyridinium ion.

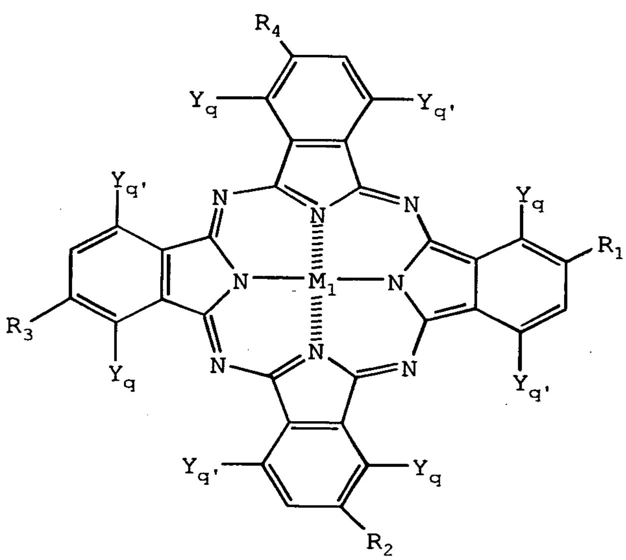
Formula (III): $M\text{-}(Y)_d$

In formula (III), M has the same meaning as M_1 in formula (5), Y represents a monovalent or divalent ligand such as halogen atom, acetate anion, acetylacetonate and oxygen, and d represents an integer of 1 to 4.

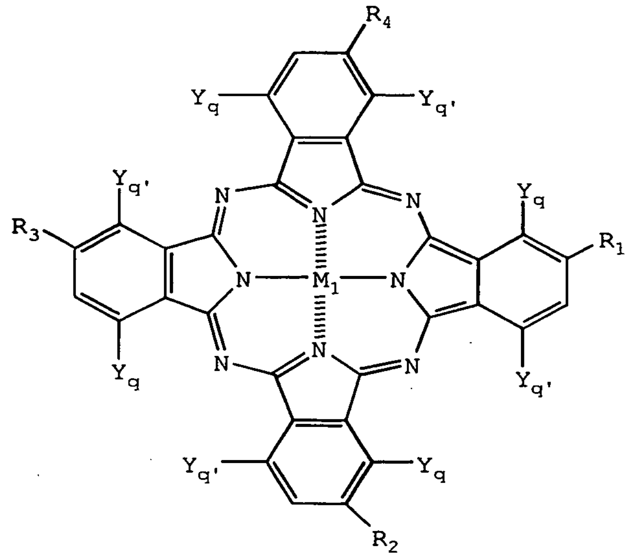
That is, according to this synthesis method, a specific number of desired substituents can be introduced. Particularly, in the case of introducing a large number of electron-withdrawing groups so as to render the oxidation potential nobler as in the present invention, this synthesis method is very excellent as compared with the methods described above for synthesizing the phthalocyanine compound of formula (2).

The thus-obtained phthalocyanine compound represented by formula (5) is usually a mixture of compounds represented by the following formulae (a)-1 to (a)-4 which are isomers in respect to the substitution site of each substituent X_p, namely, a β-position substitution type.

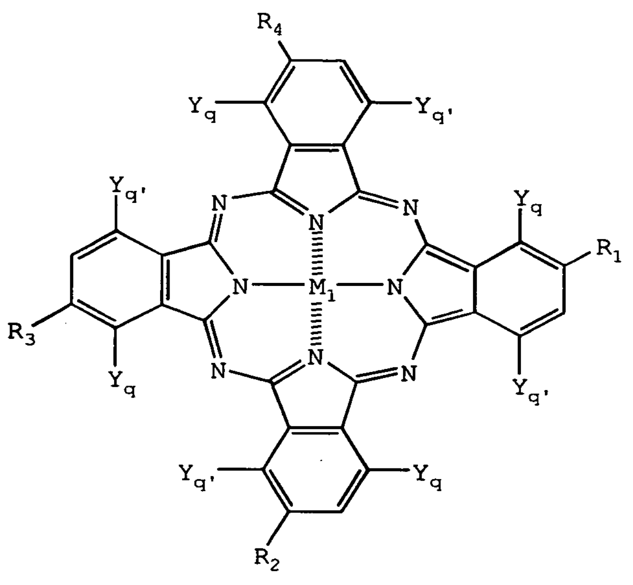
Formula (a)-1:



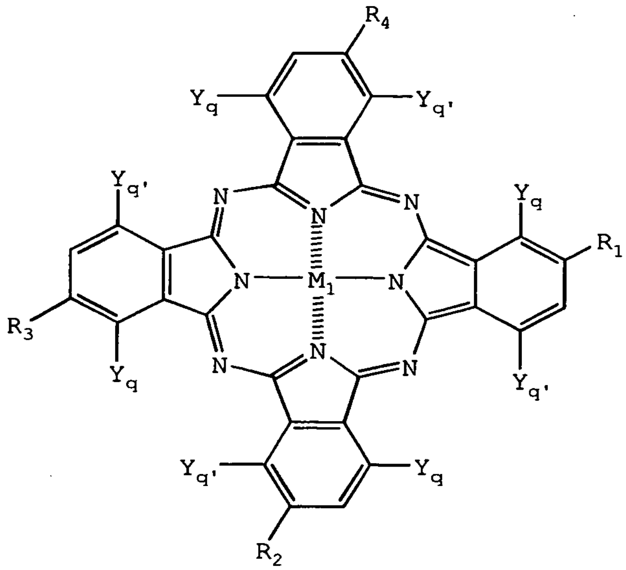
Formula (a)-2:



Formula (a)-3:



Formula (a)-4:



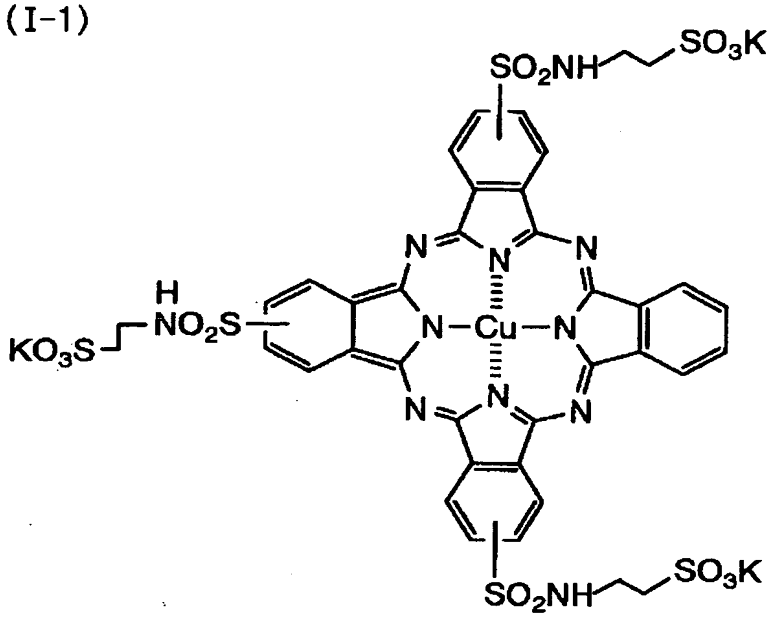
In the synthesis method above, when all X_ps are the same, a β-position substitution type phthalocyanine dye where X_{51}, X_{52}, X_{53} and X_{54} are completely the same substituents can be obtained. On the other hand, when X_ps are different, a dye having substituents of the same kind but partially different from each other or a dye having substituents different from each other can be synthesized. Among the dyes of formula (5), these dyes having electron-withdrawing substituents different from each other are preferred, because the solubility and aggregating property of dye and the aging stability of ink can be controlled.

In the present invention, it has been found to be very important for the improvement of fastness that in any substitution type, the oxidation potential is nobler than 1.0 V (vs SCE). Its great effect cannot be expected at all from the above-described known techniques. Furthermore, although the reason is not particularly known, there is a tendency that the β-position substitution type is apparently more excellent in the color hue, light fastness, ozone gas resistance and the like than the α,β-position mixed substitution type.

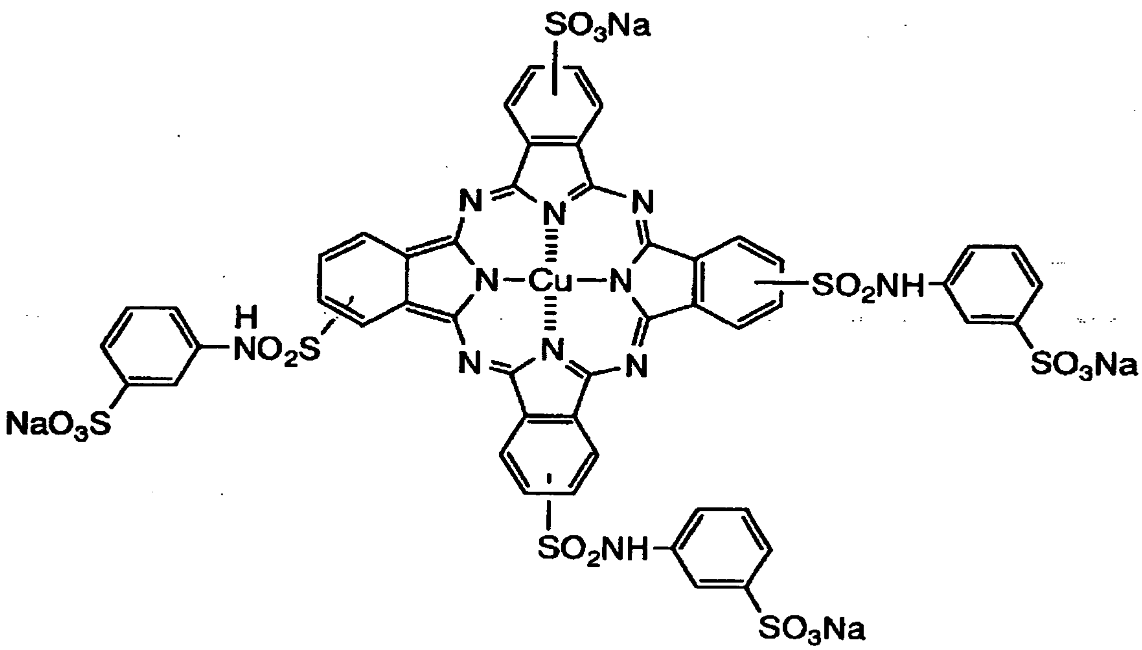
Specific examples of the phthalocyanine dyes represented by formulae (2) and (5) (Compounds I-1 to I-12 represented by formula (2) and Compounds 101 to 190 represented by formula (5)) are set forth below, however, the phthalocyanine dye for use in the present invention is not limited to the following examples.

Compound

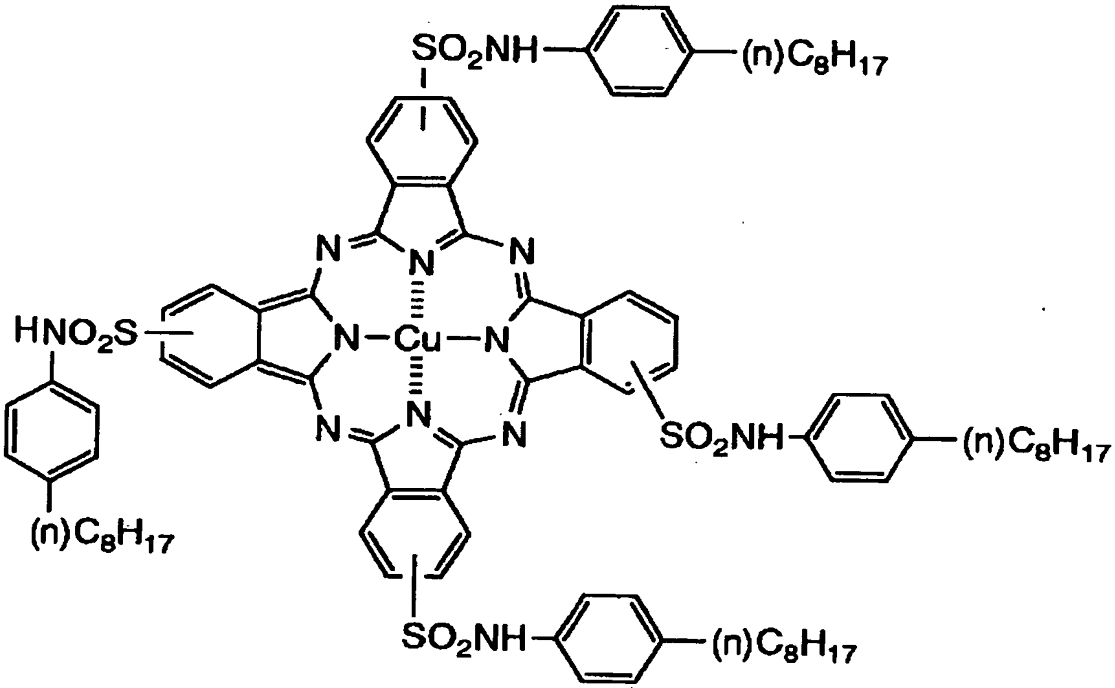
(I-1)



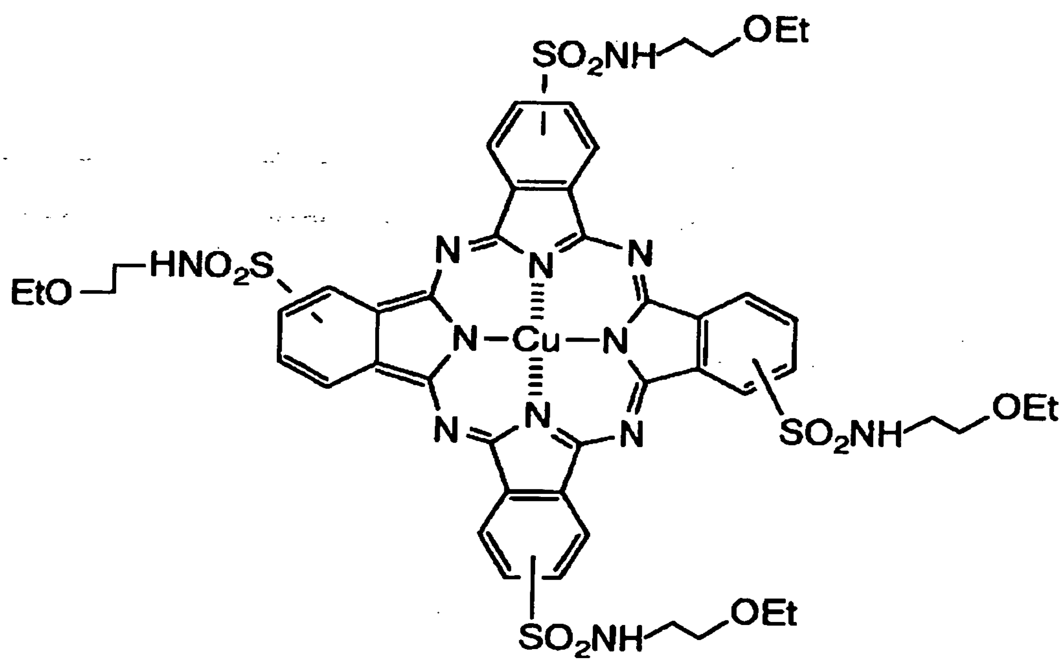
(I-2)



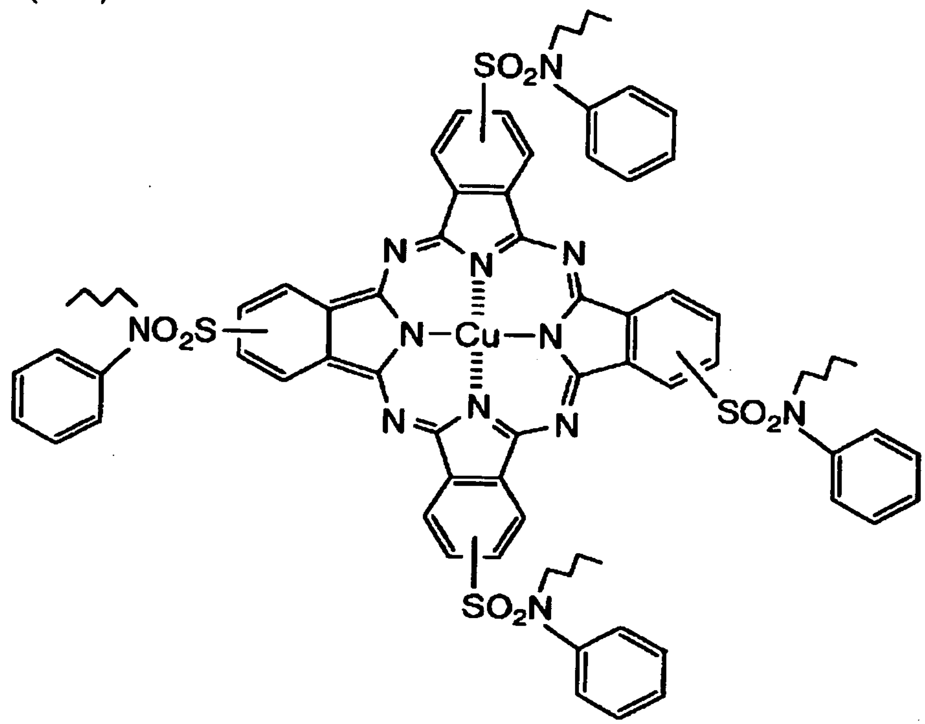
(I-3)



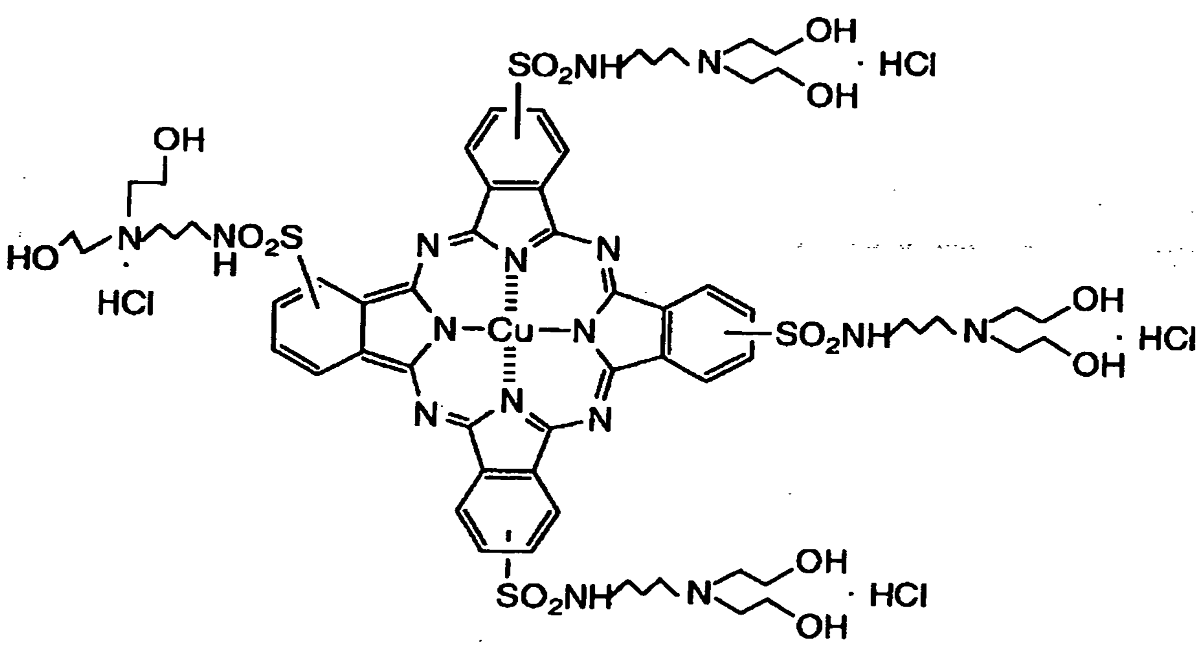
(I-4)



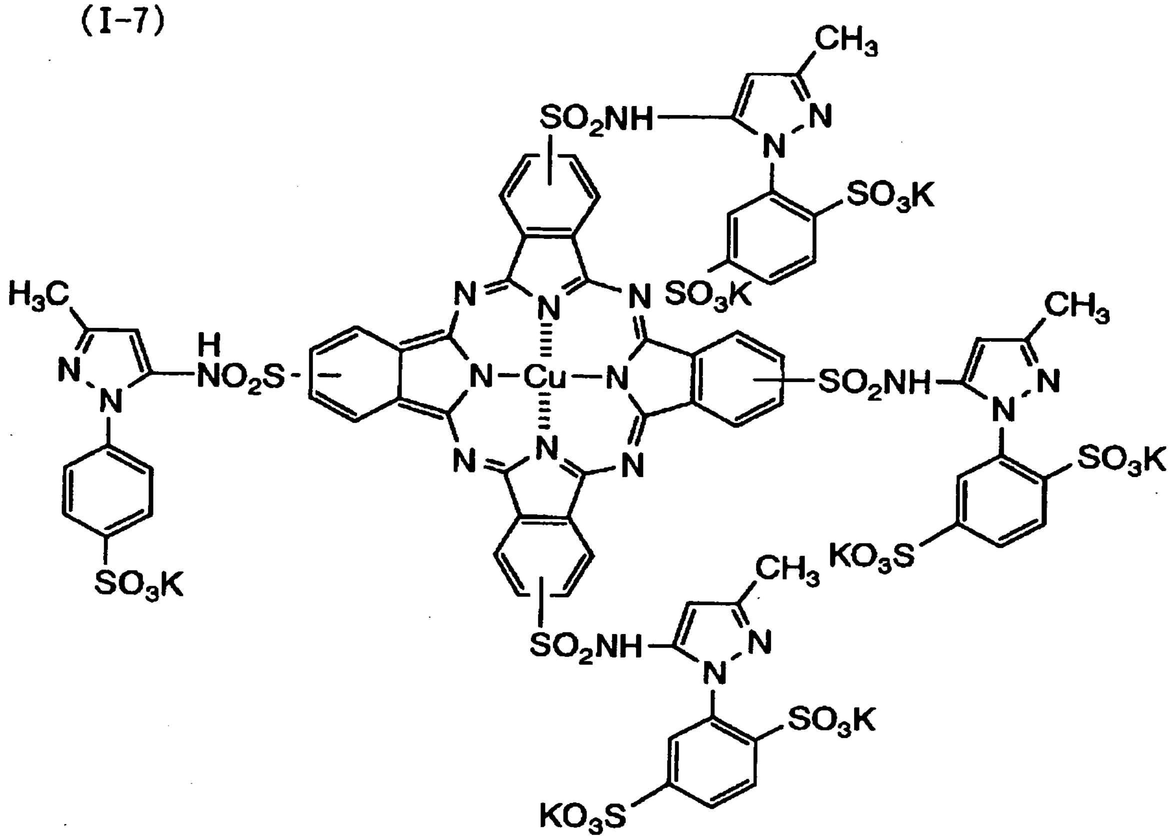
(I-5)



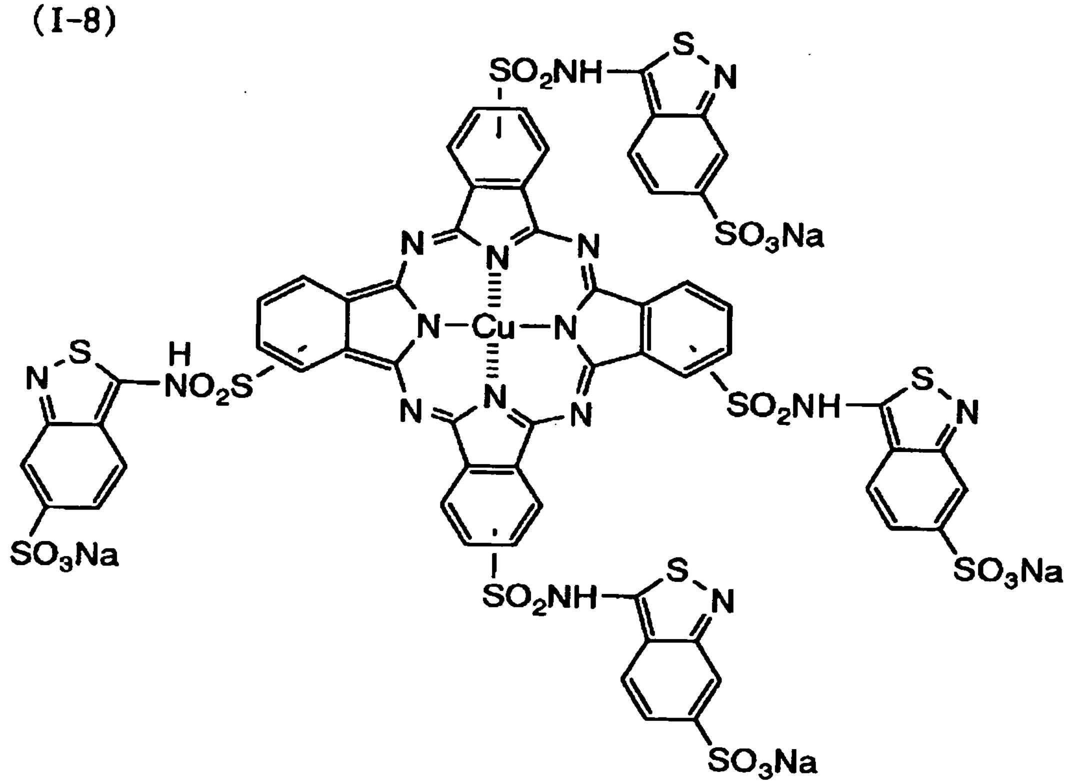
(I-6)



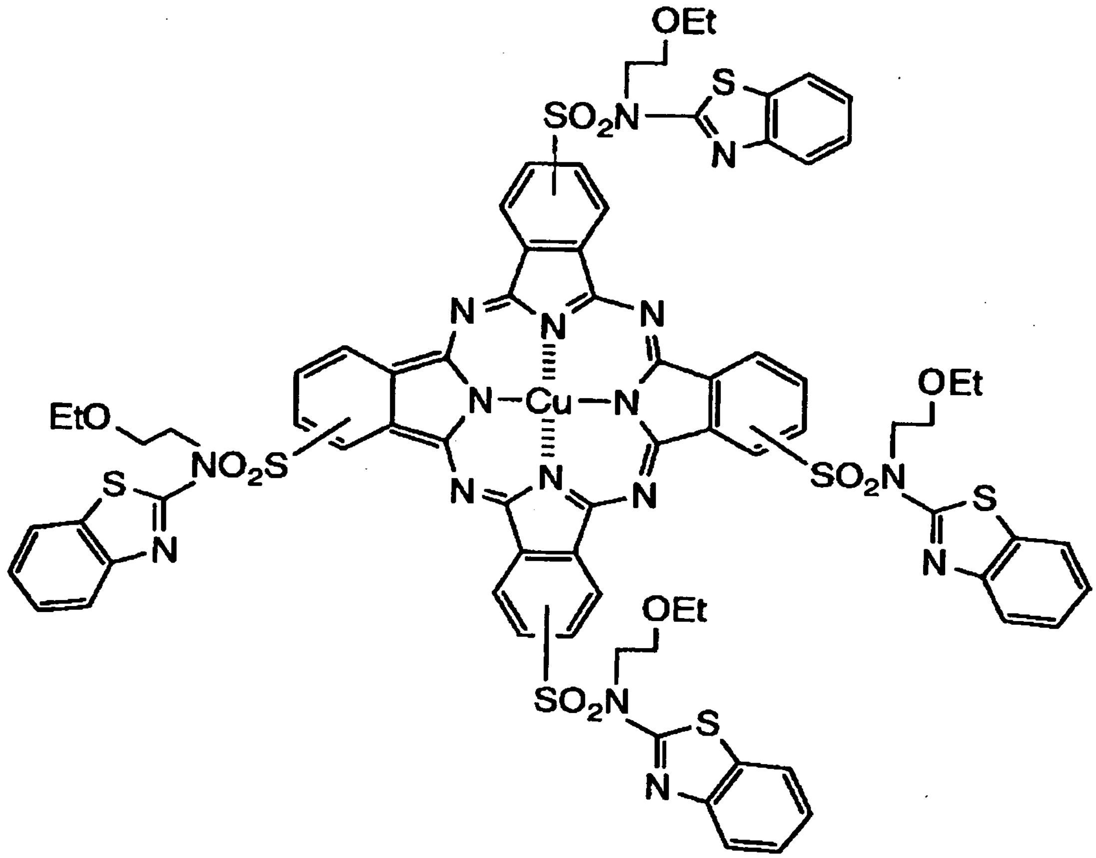
(I-7)



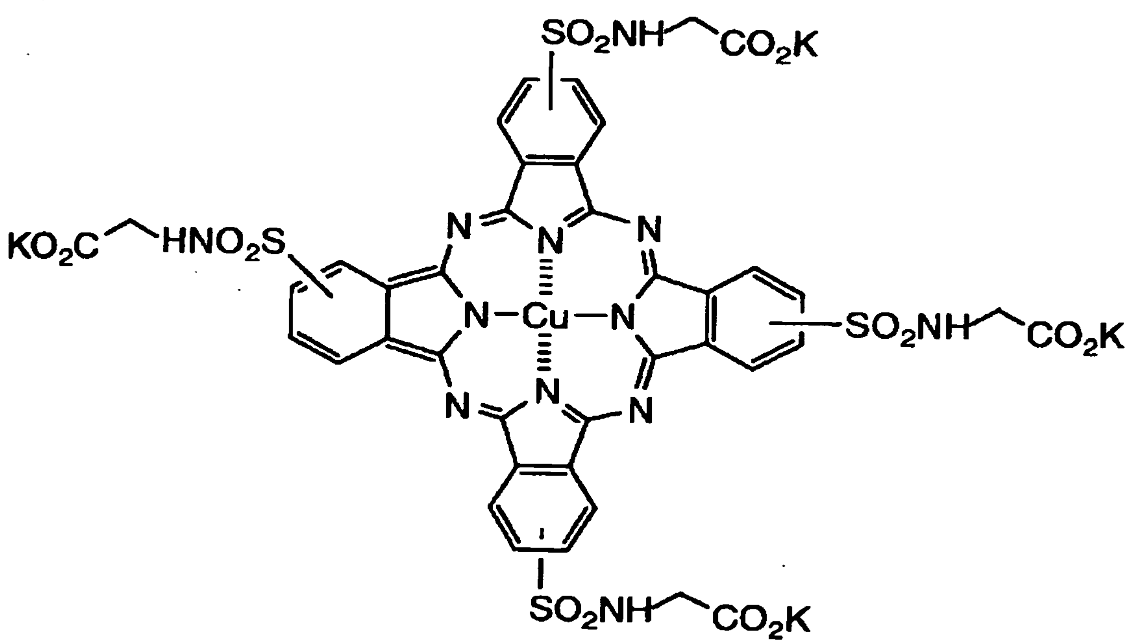
(I-8)



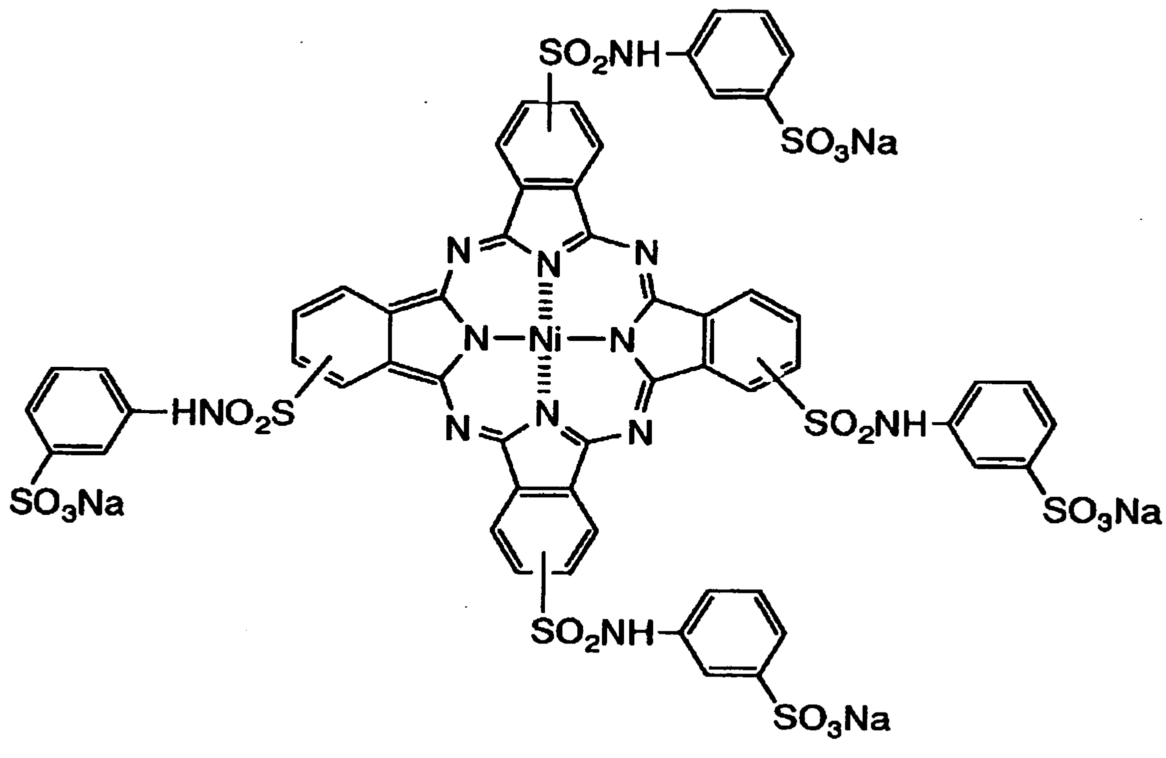
(I-9)



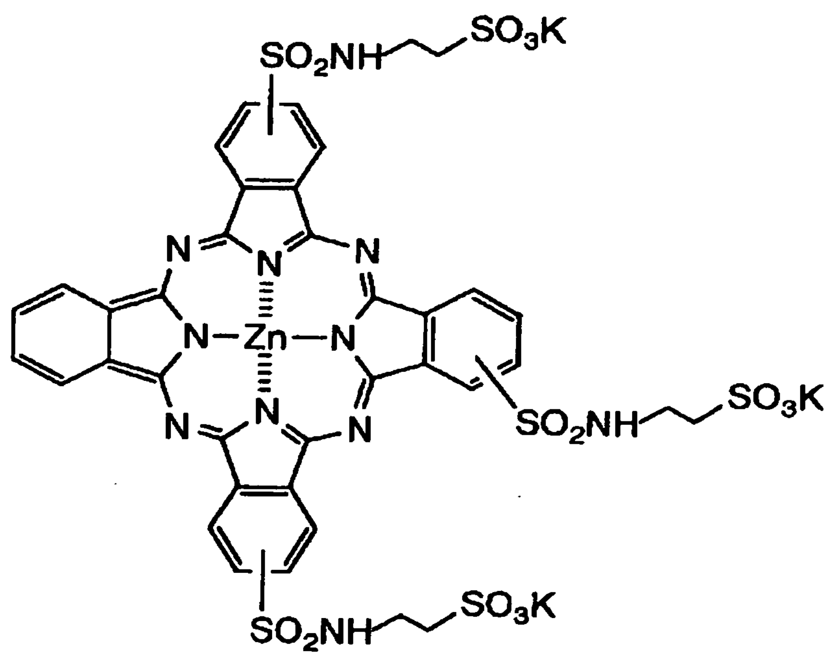
(I-10)



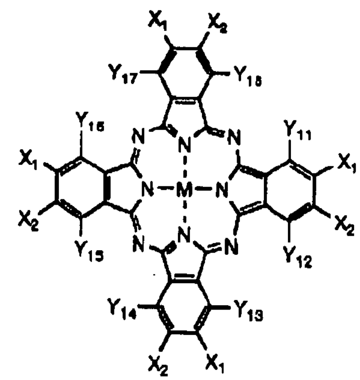
(I-11)



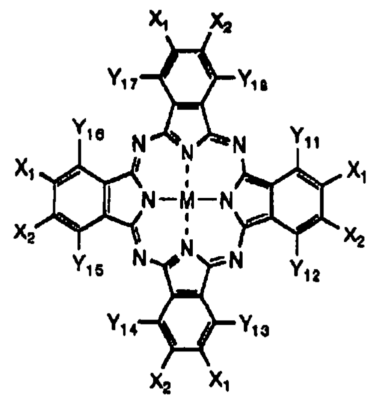
(I-12)



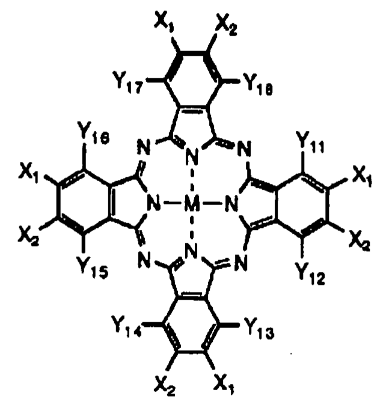
In the following Tables, specific examples of each pair of (X_1, X_2), (Y_{11}, Y_{12}), (Y_{13}, Y_{14}), (Y_{15}, Y_{16}) and (Y_{17}, Y_{18}) are independently in an irregular order.



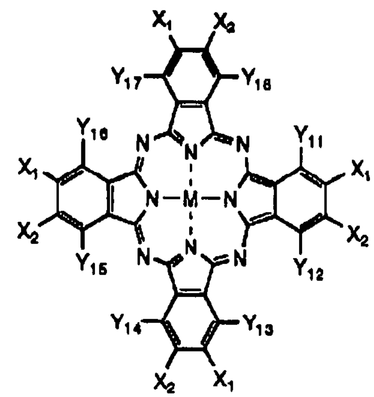
No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
101	Cu	$-SO_2-NH-CH_2-CH_2-SO_3Li$	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
102	Cu	$-SO_2-NH-CH_2-CH(OH)-CO-NH-CH_2CH_2-SO_3Na$	$-H$	$-Cl, -H$	$-Cl, -H$	$-Cl, -H$	$-Cl, -H$
103	Cu	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2NH-CH_2CH(OH)-SO_3Li$	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
104	Cu	$-SO_2-NH-C_6H_4-SO_2NH-CH_2CH_2-SO_3Li$ (p-phenylene)	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
105	Ni	$-SO_2-NH-CH_2-CH_2-CO-NH-CH(CH_2-COONa)-COONa$	$-H$	$-Cl, -H$	$-Cl, -H$	$-Cl, -H$	$-Cl, -H$
106	Cu	$-SO_2-NH-CH_2-CH_2-SO_2-NH-CH_2-COONa$	$-CN$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
107	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH(CH_2-OH)-COOLi$	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
108	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3Li$	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
109	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3K$	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$
110	Cu	$-SO_2-(CH_2)_5-CO_2K$	$-H$	$-H, -H$	$-H, -H$	$-H, -H$	$-H, -H$

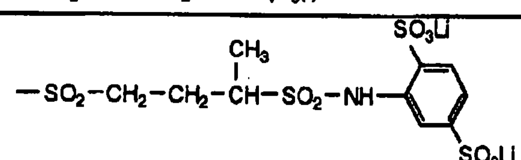


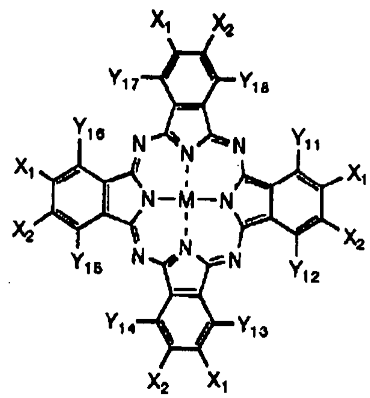
No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
111	Cu	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2-NH-CH_2CH(OH)-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
112	Cu	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2NH-CH_2-CH(OH)-CH_3$	$-SO_3Li$	-H, -H	-H, -H	-H, -H	-H, -H
113	Cu	$-SO_2-CH_2-CH(OH)-CH_2SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
114	Cu	$-SO_2-CH_2-CH(OH)-CH_3$	$-SO_3Li$	-H, -H	-H, -H	-H, -H	-H, -H
115	Cu	$-SO_2NH(CH_2)_3\overset{\oplus}{N}(CH_3)(CH_2CH_2OH)_2 \cdot CH_3-C_6H_4-SO_3^{\ominus}$	-H	-H, -H	-H, -H	-H, -H	-H, -H
116	Cu	$-CO-NH-CH_2-CH(OH)-CH_2SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
117	Cu	$-CO-NH-CH(COOLi)-CH_2CH_2SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H

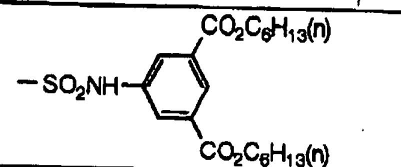
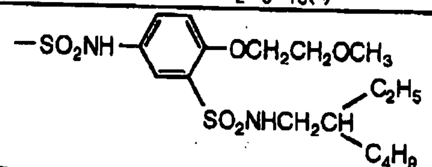
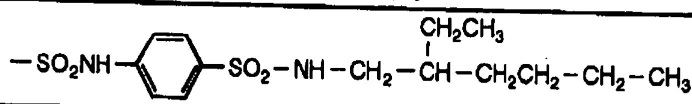
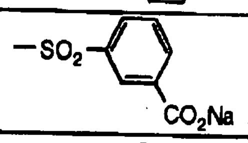
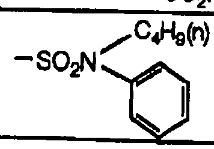


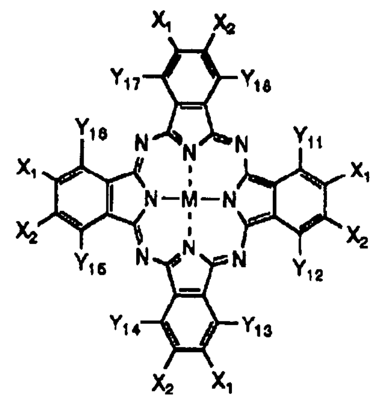
No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
118	Cu	$-SO_2CH_2CH_2CH(CH_3)SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
119	Cu	$-SO_2-CH_2-CH(OH)-CH_2-SO_3Na$	-H	-H, -H	-H, -H	-H, -H	-H, -H
120	Cu	$-SO_2-CH_2-CH_2-CH(CH_3)-COOLi$	-H	-H, -H	-H, -H	-H, -H	-H, -H
121	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH(OH)-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
122	Cu	$-CO_2CH_2CH_2CH_2SO_2-NH-CH_2-CH(OH)-CH_2-SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H
123	Cu	$-SO_2NH-C_8H_{17}(t)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
124	Cu	$-SO_2-NH-CH_2-CH(CH_2CH_3)-CH_2CHCH_2-CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H

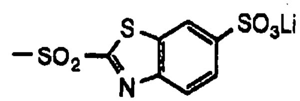
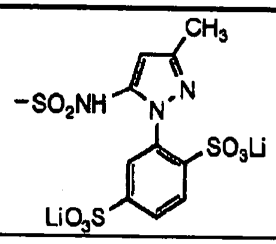
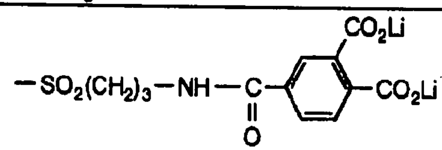
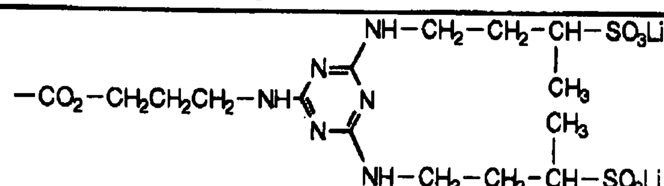


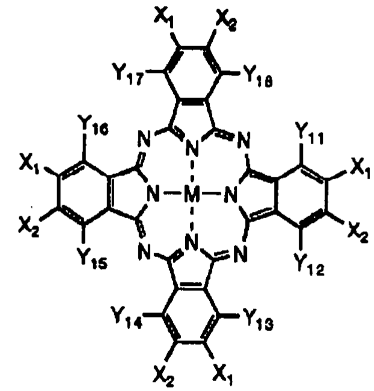
No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
125	Cu	$-SO_2CH_2CH_2CH_2SO_2-NH-CH_2-CH(CH_3)-CH_2-CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
126	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-CH(CH_3)-CH_2-O-CH_3$	-H	-H, -H	-H, -H	-H, -H	-H, -H
127	Cu	$-SO_2CH_2CH_2CH_2SO_2NHCH_2CH_2CH_2O-CH(CH_3)_2$	-H	-H, -H	-H, -H	-H, -H	-H, -H
128	Zn	$-SO_2-CH_2-CH(O-CH_3)-CH_2-O-CH_3$	-CN	-H, -H	-H, -H	-H, -H	-H, -H
129	Cu	$-CO-NH-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2CH_3$	-H	-Cl, -H	-Cl, -H	-Cl, -H	-Cl, -H
130	Cu	$-CO_2-CH(CH_3)-CH_2-O-C_4H_9(t)$	-H	-H, -H	-H, -H	-H, -H	-H, -H
131	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H

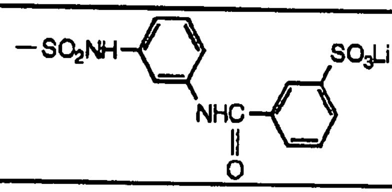
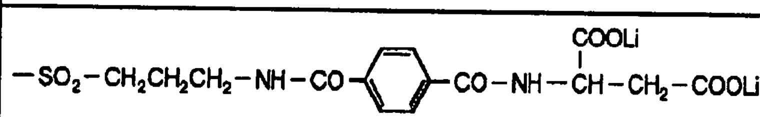


No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
132	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
133	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
134	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
135	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
136	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H



No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
137	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
138	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
139	Cu		-Cl	-H, -H	-H, -H	-H, -H	-H, -H
140	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H



No.	M	X_1	X_2	Y_{11}、Y_{12}	Y_{13}、Y_{14}	Y_{15}、Y_{16}	Y_{17}、Y_{18}
141	Cu	$-SO_2NH-CH(COONa)-CH_2-CO-N-(CH_2CH_2OH)_2$	-H	-H, -H	-H, -H	-H, -H	-H, -H
142	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
143	Cu	$-CO-NH-CH_2-CH(OH)-CO-NH-CH(COOK)-CH_2CH_2-SO_3K$	-H	-H, -H	-H, -H	-H, -H	-H, -H
144	Cu		-H	-H, -H	-H, -H	-H, -H	-H, -H
145	Cu	$-SO_2CH_2CH_2OCH_2CH_2OCH_2CH_2SO_3Li$	-H	-H, -H	-H, -H	-H, -H	-H, -H

In the following Tables, each introduction site of substituents (R_1) and (R_2) is in an irregular order within the β-position substitution type.

$M\text{-}Pc(R_1)_m(R_2)_n$

No.	M	R_1	m	R_2	n
146	Cu	$-SO_2-NH-CH_2-CH(CH_3)-SO_3Li$	3	$-SO_2-NH-CH_2-CH(OH)-CH_3$	1
147	Cu	$-SO_2-NH-CH_2-CH_2SO_3Li$	3	$-SO_2-NH-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	1
148	Cu	$-SO_2-NH-CH_2-CH(CH_3)-SO_3Li$	3	$-SO_2NH-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH_2-O-CH_2-CH_2-OH$	1
149	Cu	$-SO_2-NH-CH_2-CH(CH_3)-SO_3Li$	2	$-SO_2-NH-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$	2
150	Cu	$-SO_2-NH-CH_2-CH_2-SO_2-NH-CH_2CH_2-COONa$	3	$-SO_2NH-CH(CH_3)-CH_2OH$	1
151	Cu	$-SO_2-NH-C_6H_4-SO_2NH-CH_2-CH(OH)-SO_3Li$	3	$-SO_2NH-CH_2-CH_2-O-CH_2-CH_2-OH$	1
152	Cu	$-SO_2-CH_2-CH_2-CH(CH_3)-SO_3Li$	2.5	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-OH$	1.5
153	Cu	$-SO_2-CH_2-CH_2-CH(CH_3)-SO_3Na$	2	$-SO_2-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$	2
154	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3Li$	3	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	1
155	Cu	$-SO_2-CH_2-CH_2-CH_2-COOK$	2	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_2-COOK$	2
156	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_3Li$	3	$-SO_2-CH_2-CH(OH)-CH_2-SO_3Li$	1
157	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-SO_3Li$	2	$-SO_2-CH_2-CH_2-CH_2-CO_2-CH_2-CH_2-CH(OH)-CH_2-COOK$	2

$M-Pc(R_1)_m(R_2)_n$

No.	M	R_1	m	R_2	n
158	Cu	$-SO_2-CH_2-CH(OH)-CH_2-SO_3Li$	3	$-SO_2-CH_2-C_6H_4-SO_2NH-CH_2-CH(OH)-CH_2-OH$	1
159	Cu	$-SO_2NHCH_2CH_2-SO_3Li$	3	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	1
160	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-SO_3Na$	3	$-SO_2-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-COONa)-CH_2-COONa$	1
161	Cu	$-SO_2CH_2CH_2CH_2SO_3Li$	3	$-SO_2CH_2CH_2CH_2SO_2NHCH_2-CH(OH)-CH_2SO_3Li$	1
162	Cu	$-SO_2CH_2CH_2CH_2SO_3Li$	2	$-SO_2CH_2CH_2OCH_2CH_2OCH_2CH_2OH$	2
163	Cu	$-SO_2CH_2CH_2CH_2SO_3K$	3	$-SO_2CH_2CH_2CH_2SO_2NH-CH(CH_3)-CH_2-OH$	1
164	Cu	$-SO_2CH_2CH_2CH_2SO_3Li$	2	$-SO_2CH_2CH_2CH_2SO_2N(CH_2CH_2OH)_2$	2
165	Cu	$-CO-NH-CH_2-CH_2-SO_3K$	3	$-CO-NH-CH_2-CH_2-O-CH_2-CH_2-OH$	1
166	Cu	$-CO-NH-CH_2-CH_2-SO_2-NH-CH_2-CH_2-COONa$	3	$-CO-NH-CH_2-CH(OH)-CH_3$	1
167	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH(OH)-CH_2CO_2Li$	2.5	$-CO-NH-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$	1.5
168	Cu	$-CO_2-CH_2-CH_2-CH(CH_3)-SO_3Na$	2	$-CO-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-OH)_2$	2
169	Cu	$-CO_2-CH_2-CH_2-CH_2-SO_3Li$	3	$-CO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	1
170	Cu	$-CO_2-CH_2-CH_2-CH_2COOK$	2	$-CO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_2-COOK$	2

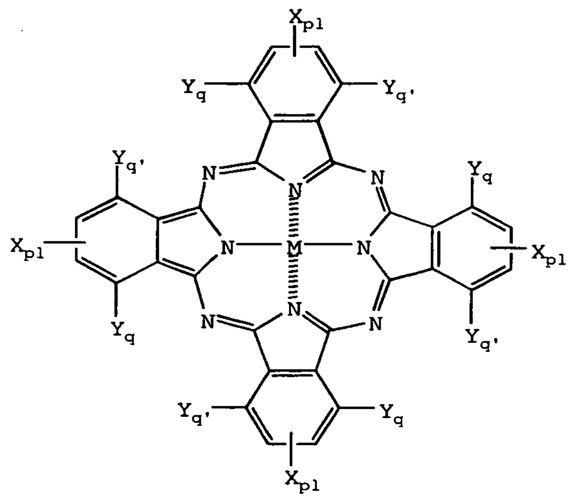
$M\text{-}Pc(R_1)_m(R_2)_n$

No.	M	R_1	m	R_2	n
171	Cu	$-CO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-SO_3Na$	3	$-CO_2-CH_2-C_6H_4-SO_2NH-CH_2-CH(OH)-CH_2-OH$	1
172	Cu	$-SO_2CH_2CH_2OCH_2CH_2O-CH_2CH_2SO_3K$	2	$-CO_2-CH_2-CH_2-CH_2-CO_2-CH_2-CH_2-CH(OH)-CH_2-COOK$	2
173	Cu	$-SO_2(CH_2)_3SO_2NHCH_2CH(OH)CH_2OH$	2	$-CO_2-CH_2-CH(OH)-CH_2-SO_3Li$	2
174	Cu	$-SO_2(CH_2)_3SO_2NHCH_2-CH(OH)-CH_2SO_3K$	3	$-CO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	1
175	Cu	$-SO_2(CH_2)_3SO_2NH(CH_2)_3N(CH_2CH_2OH)_2$	2	$-CO_2-CH_2-CH_2-CH_2-CO-N(CH_2-CH_2-COOLi)-CH_2-COOLi$	2
176	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(CH_2CH_3)-CH_2CH_2-CH_2CH_3$	1
177	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$	2	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	1
178	Cu	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$	3	$-SO_2-CH_2-CH_2-CH_2-CO_2-CH_2-CH(CH_2CH_3)-CH_2CH_2-CH_2CH_3$	1
179	Cu	$-SO_2-CH_2-CH(CH_2CH_3)-CH_2CH_2-CH_2CH_3$	2	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(O-CH_3)-CH_3$	2
180	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(O-CH_3)-CH_3$	3	$-SO_2NH-CH_2-CH_2-SO_2NH-CH_2-CH_2-O-CH_2-CH_2-OH$	1
181	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	3	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH-(CH_3)_2$	1
182	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2NH-CH_2-CH(OH)-CH_3$	2.5	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	1.5

$M\text{-}Pc(R_1)_m(R_2)_n$

No.	M	R_1	m	R_2	n
183	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	2	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-(CH_2)_3-CH_2-O-CH_2CH_2-OH$	2
184	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$	1
185	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH_2-CH(OH)-CH_3$	3	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$	1
186	Cu	$-SO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	3	$-SO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH$	1
187	Cu	$-SO_2-CH_2-CH_2-CH_2-SO_2-NH-CH-(CH_3)_2$	3	$-CO_2-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2CH_3$	1
188	Cu	$-CO_2-CH_2-CH_2-CH_2-CO_2-NH-CH(CH_3)-CH_2-CH_3$	3	$-CO_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$	1
189	Cu	$-CO-NH-CH_2-CH_2-SO_2-NH-CH-(CH_3)_2$	3	$-SO_2-NH-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2-CH_3$	1
190	Cu	$-CO-NH-CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2CH_3$	3	$-CO-NH-CH_2-CH_2-O-CH_2-CH_2-O-CH_3$	1

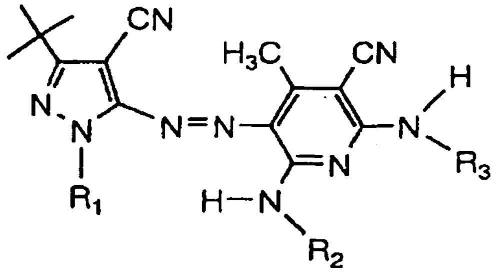
The structure of the phthalocyanine compound represented by $M\text{-}Pc(X_{p1})_m(X_{p2})_n$ Compound Nos. 146 to 190 is shown below:

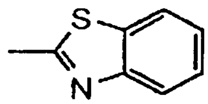
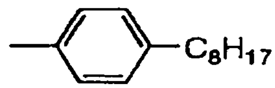
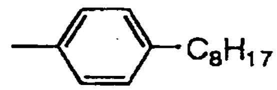
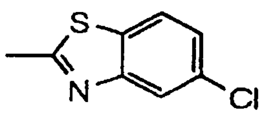
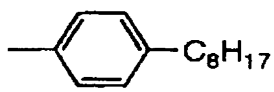
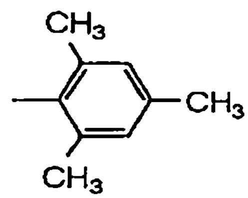
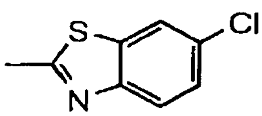
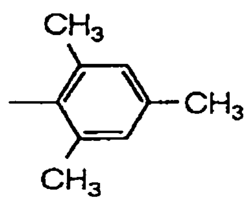
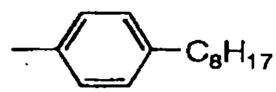
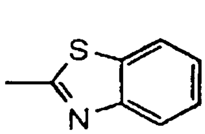
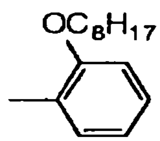
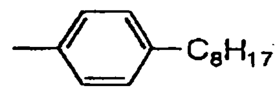
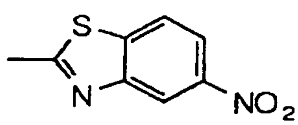
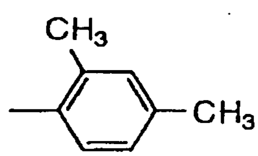
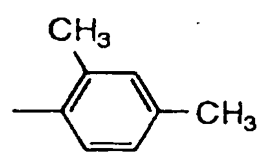


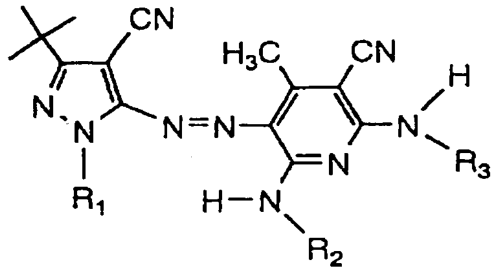
(wherein each X_{p1} is independently X_{p1} or X_{p2}).

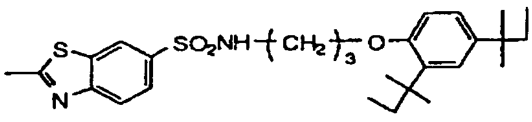
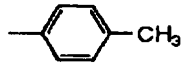
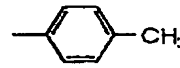
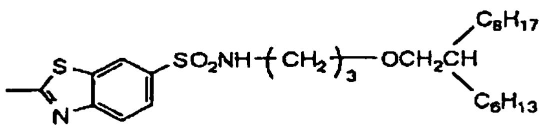
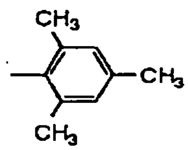
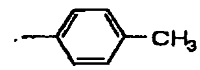
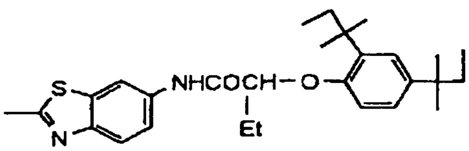
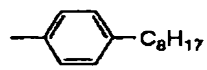
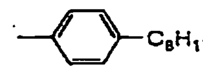
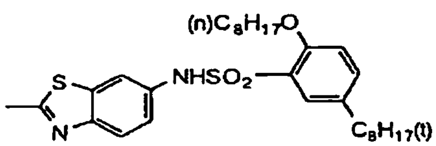
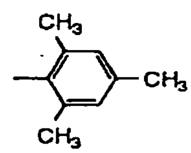
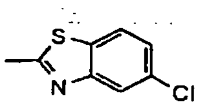
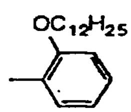
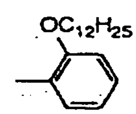
The phthalocyanine dye represented by formula (2) can be synthesized according to the patent publications described above. Furthermore, the phthalocyanine dye represented by formula (5) can be synthesized by the methods described in JP-A-2001-226275, JP-A-2001-96610, JP-A-2001-47013 and JP-A-2001-193638, in addition to the synthesis method described above. The starting material, dye intermediate and synthesis route are not limited to those described in these patent publications.

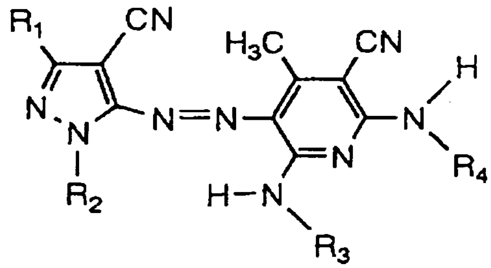
Specific examples of the azo dyes represented by formulae (1) and (3), particularly the azo dyes in which two heterocyclic groups are directly connected to an azo group are set forth below. These magenta dyes are used in the magenta ink and light magenta ink and further are used as one of constituent inks in the dark yellow ink and black ink.

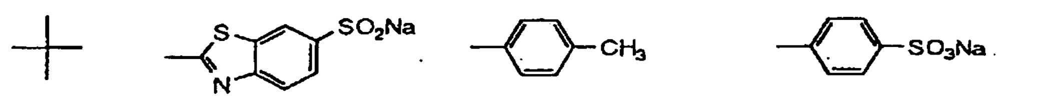
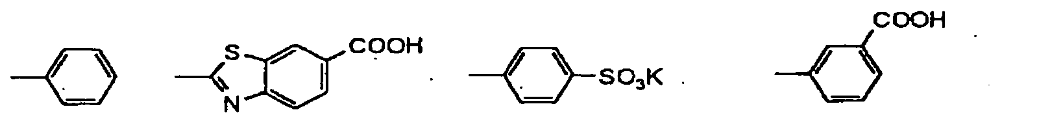
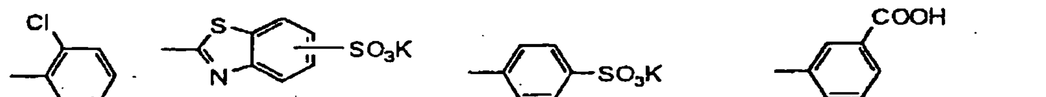
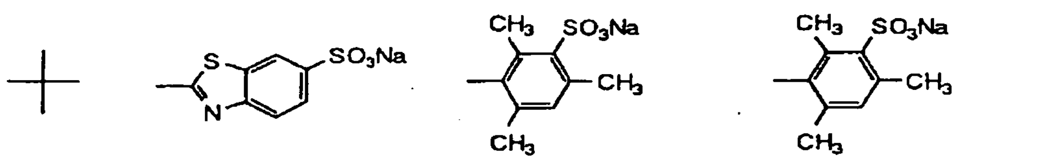
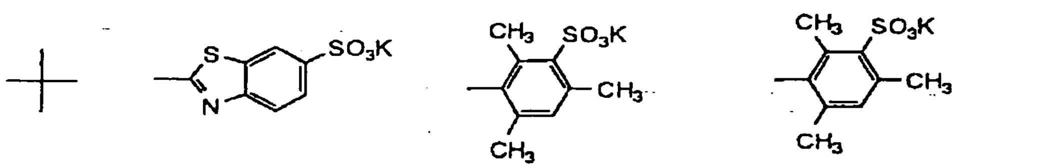
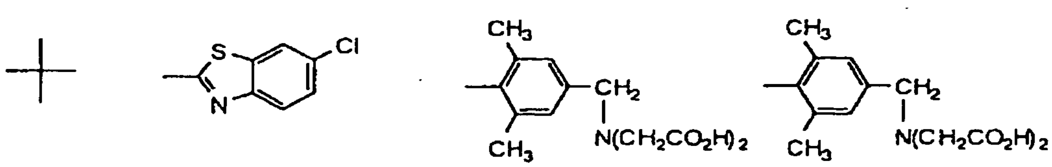
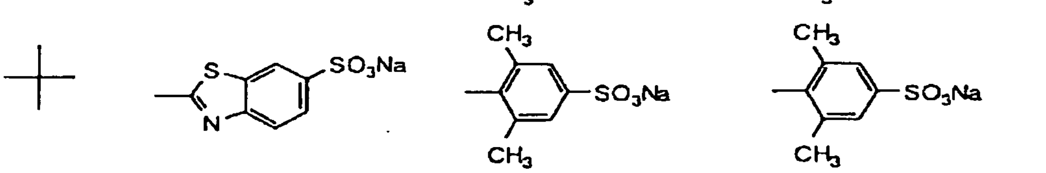


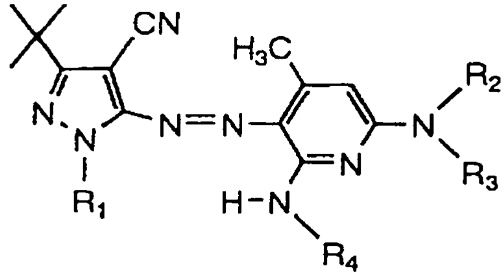
Dye	R_1	R_2	R_3
a–1			
a–2			
a–3			
a–4			
a–5			

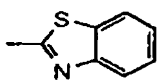
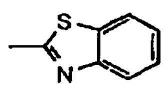
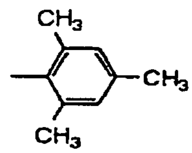
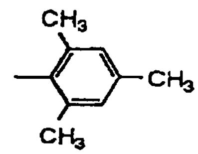
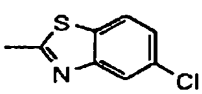
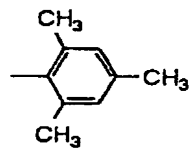
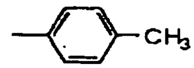
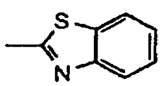
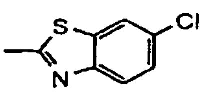
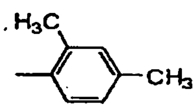
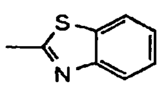
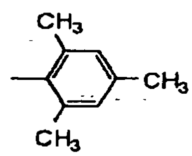
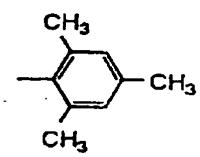
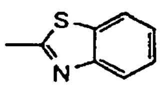
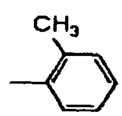
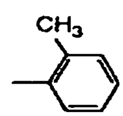
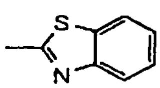
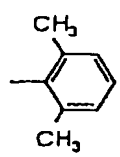
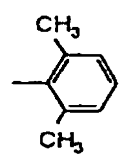
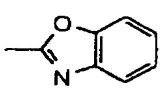
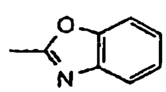
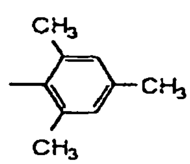
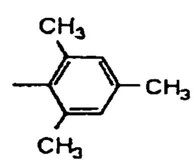


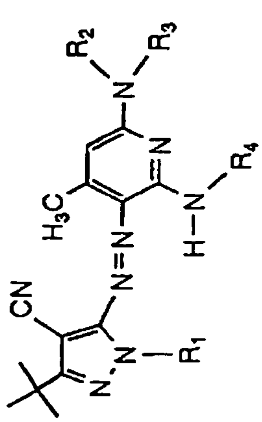
Dye	R_1	R_2	R_3
a-6			
a-7			
a-8			
a-9			$C_8H_{17}(t)$
a-10			

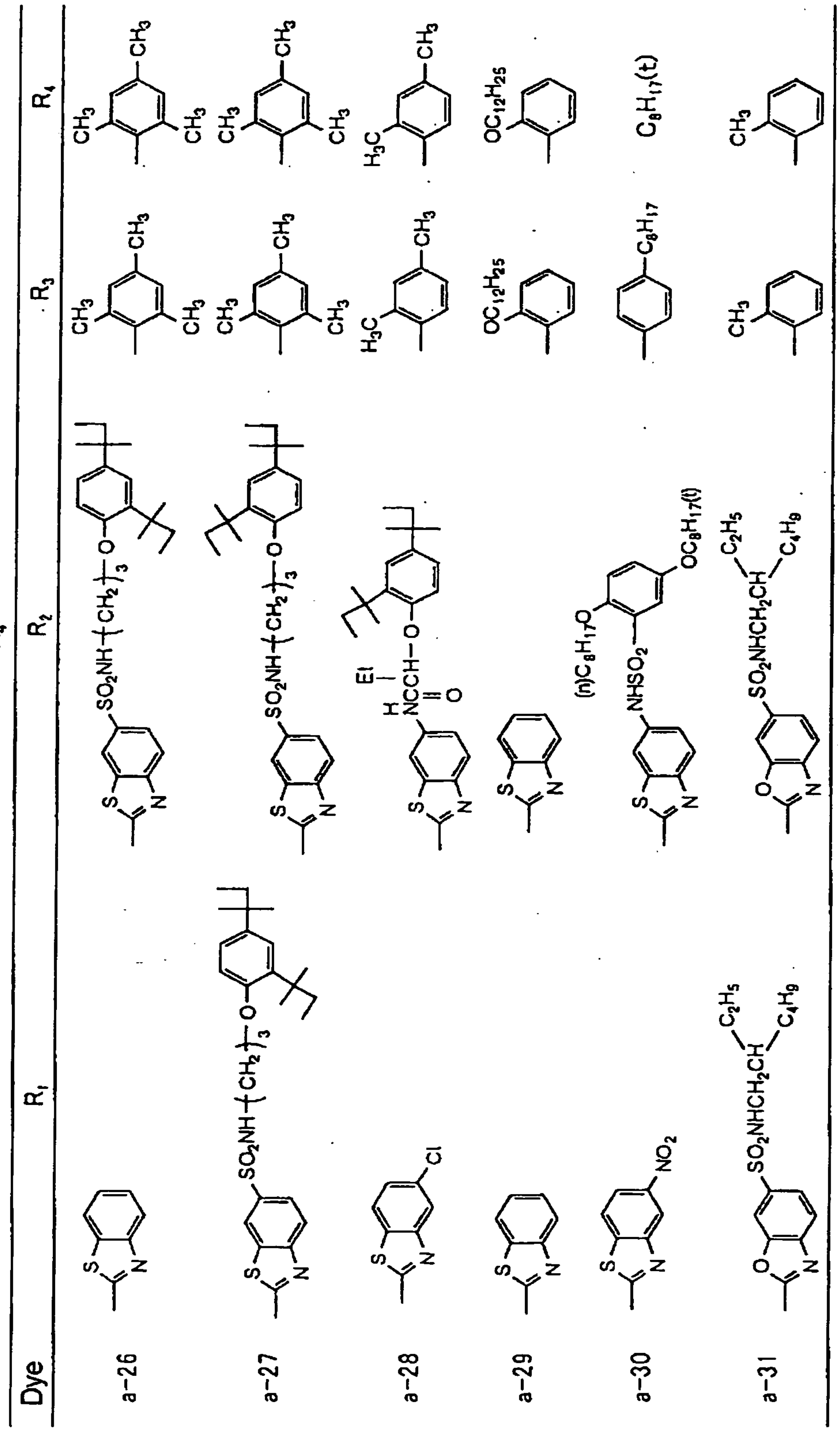


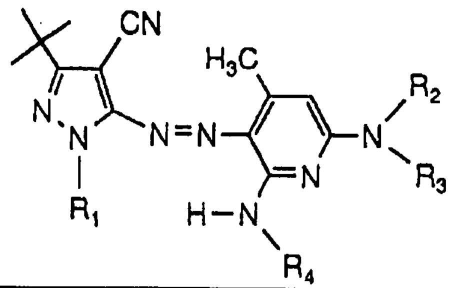
Dye	R_1 / R_2 / R_3 / R_4
a-11	
a-12	
a-13	 (4,5-mix)
a-14	
a-15	
a-16	
a-17	

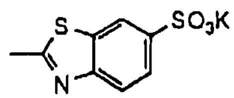
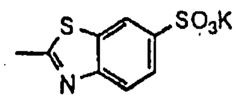
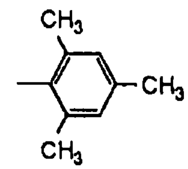
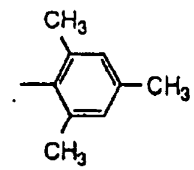
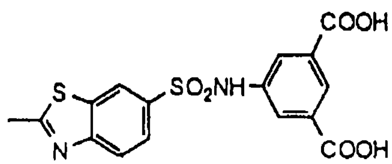
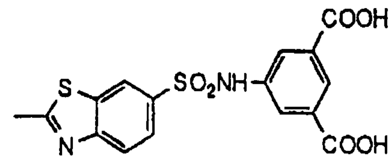
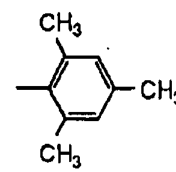
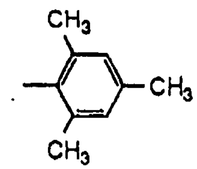
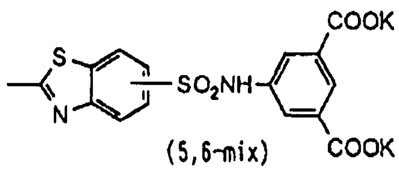
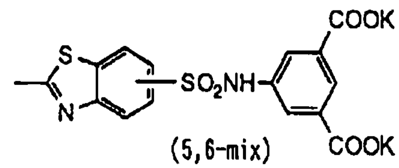
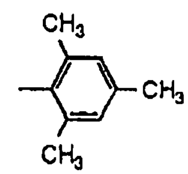
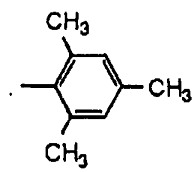
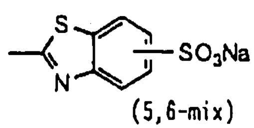
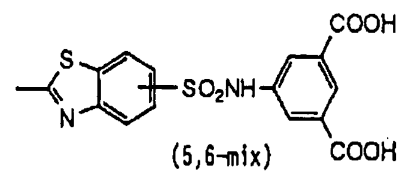
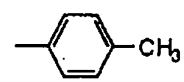
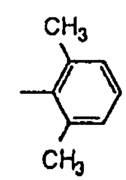


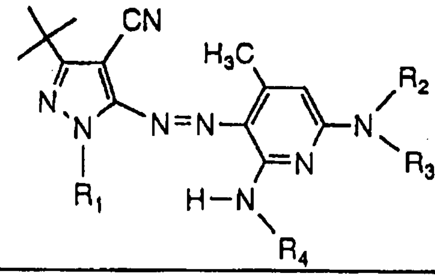
Dye	R_1	R_2	R_3	R_4
a-18				
a-19		$-SO_2CH_3$		
a-20		$-COCH_3$	$C_8H_{17}(t)$	$C_8H_{17}(t)$
a-21		$-SO_2CH_3$		$C_8H_{17}(t)$
a-22		H		
a-23		H		
a-24		H		
a-25				

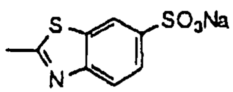
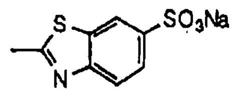
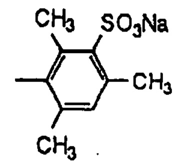
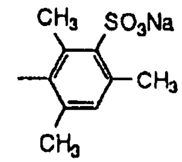
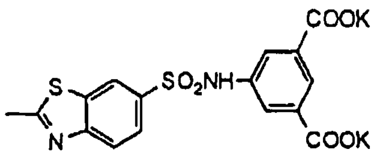
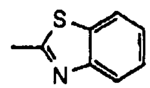
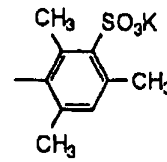
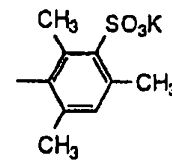
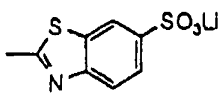
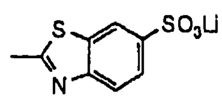
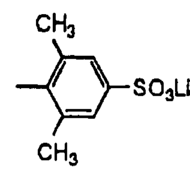
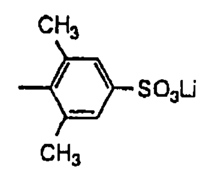
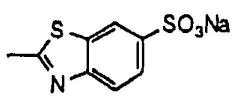
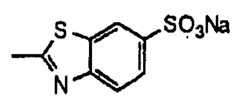
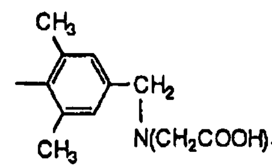
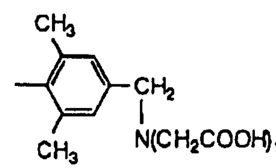
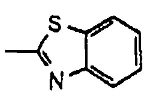
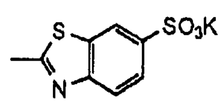
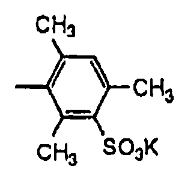
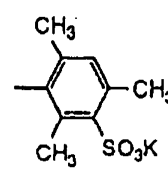


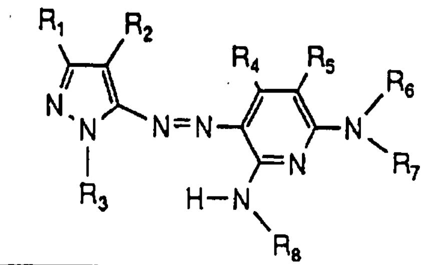

Dye
R1
R2
R3
R4
a-26
a-27
a-28
a-29
a-30
a-31

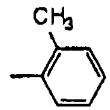
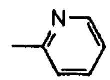
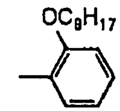
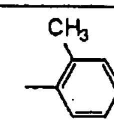
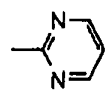
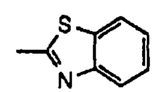
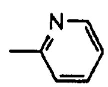
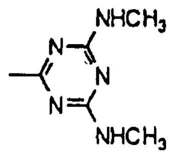
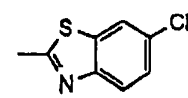
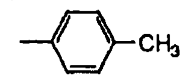
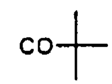
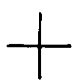
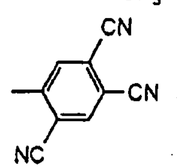
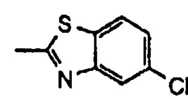
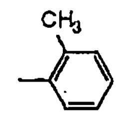
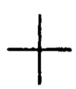
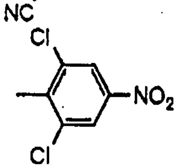
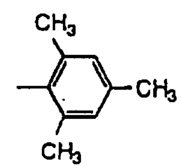
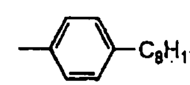
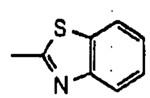
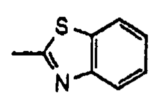
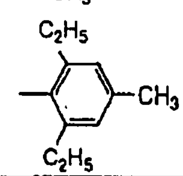
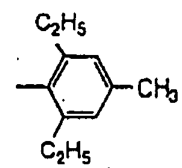


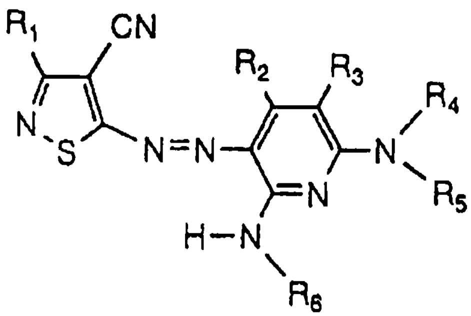
Dye	R_1	R_2	R_3	R_4
a-32				
a-33				
a-34				
a-35				

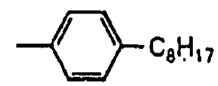
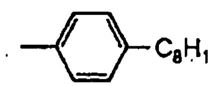
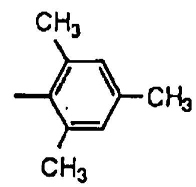
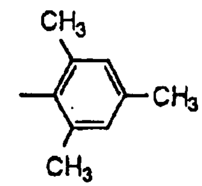
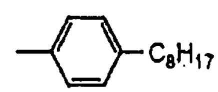
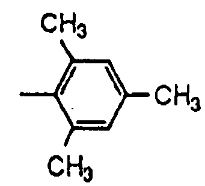
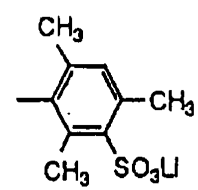
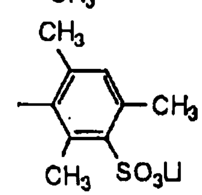
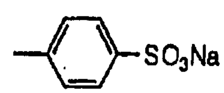
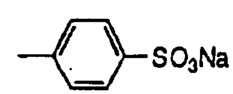


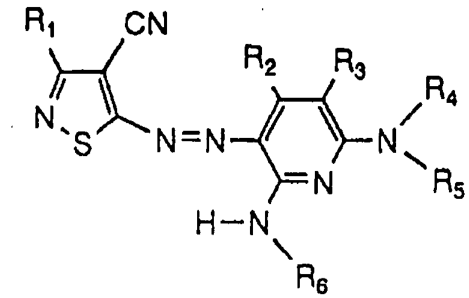
Dye	R_1	R_2	R_3	R_4
a-36				
a-37				
a-38				
a-39				
a-40				

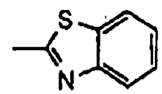
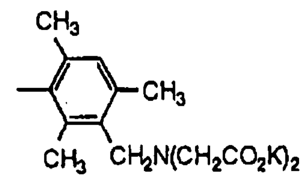
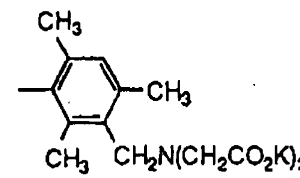
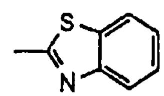
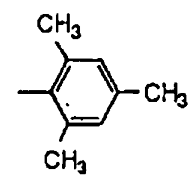
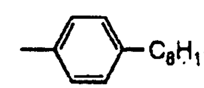
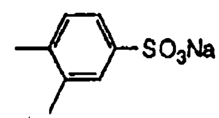
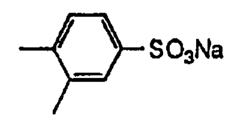


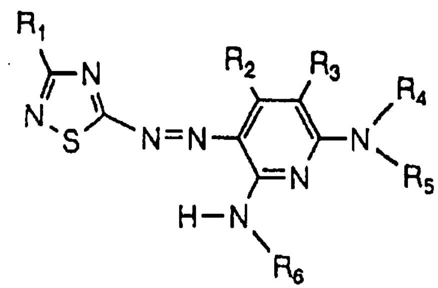
Dye	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
a-41		CN		H	$CONH_2$	SO_2CH_3		
a-42		Br		COOEt	H		$C_8H_{17}(t)$	$COCH_3$
a-43		SO_2CH_3		$CONH_2$	H			
a-44		CN		H	H			SO_2CH_3
a-45		Br		H	$CONH_2$	$\underset{\underset{O}{\Vert}}{C}CH_3$		
a-46		CN		CH_3	H			

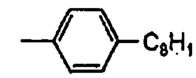
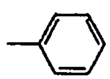
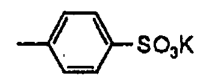
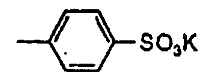
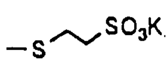
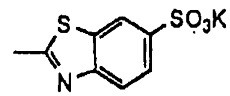
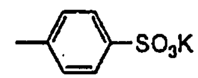
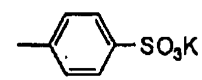
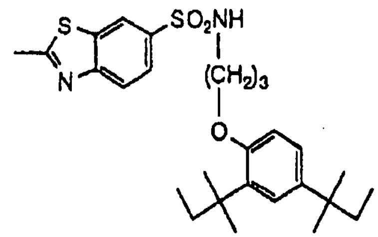
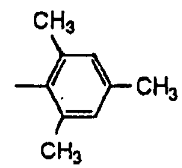
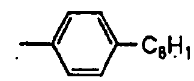
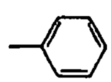
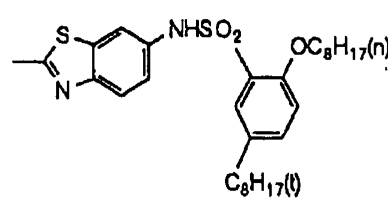
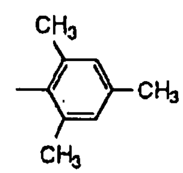


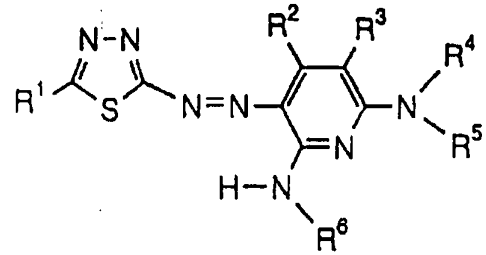
Dye	R_1	R_2	R_3	R_4	R_5	R_6
b-1	CH_3	CH_3	CN	H		
b-2	CH_3	CH_3	CN	H		
b-3	CH_3	CH_3	$CONH_2$	H		
b-4	CH_3	CH_3	H	H		
b-5	CH_3	H	CN	H		

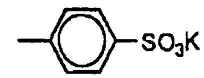
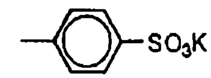
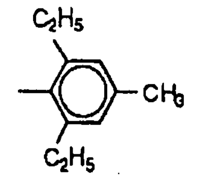
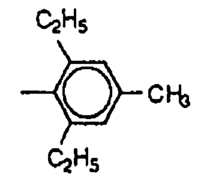
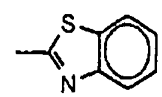
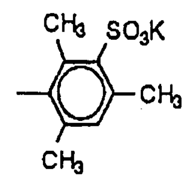
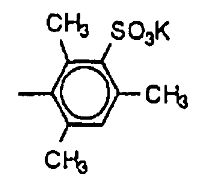
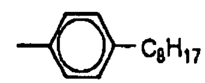
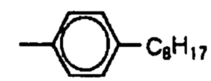
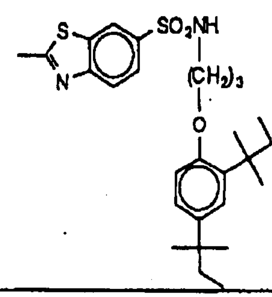
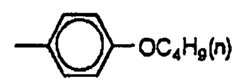
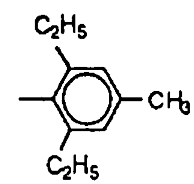


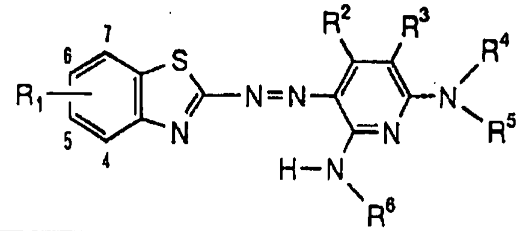
Dye	R_1	R_2	R_3	R_4	R_5	R_6
b-6	CH_3	CH_3	H			
b-7	CH_3	CH_3	H			
b-8	CH_3	H	H	SO_2CH_3		

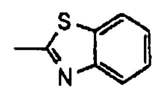
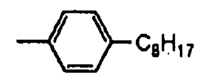
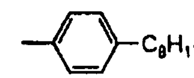
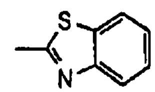
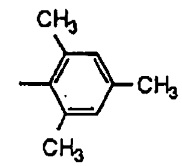
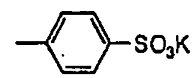
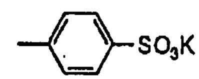
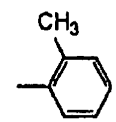
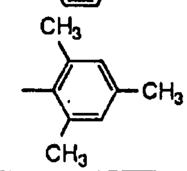


Dye	R_1	R_2	R_3	R_4	R_5	R_6
c-1	$-SCH_3$	CH_3	CN	H	$C_8H_{17}(t)$	
c-2		H	$CONH_2$	H		
c-3		CH_3	H			
c-4	$-CH_3$	CH_3	H			
c-5		H	H			$C_8H_{17}(t)$

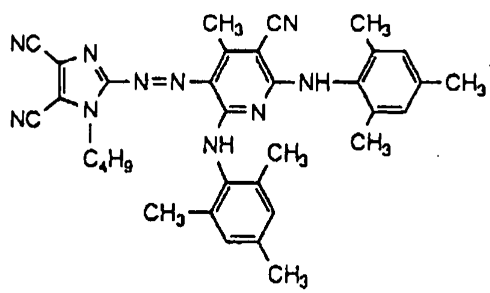


Dye	R_1	R_2	R_3	R_4	R_5	R_6
d-1	Me	CH_3	CN	H		
d-2	Me	CH_3	CN	H		
d-3	Me	H	H			
d-4	Ph	CH_3	$CONH_2$	H		
d-5	Ph	CH_3	H			

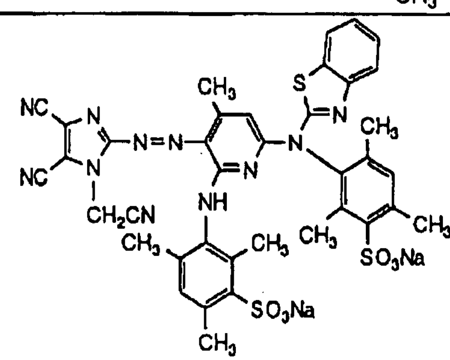


Dye	R_1	R_2	R_3	R_4	R_5	R_6
e-1	5-Cl	CH_3	$CONH_2$	H	$C_8H_{17}(t)$	$C_8H_{17}(t)$
e-2	5,6-diCl	H	H			
e-3	5,6-diCl	CH_3	H			$COCH_3$
e-4	5-CH_3	H	CN	H		
e-5	5-NO_2	CH_3	H	SO_2CH_3		

f-1



f-2



The dye of the present invention fulfilling the above-described requirement of molar extinction coefficient ratio further has an oxidation potential preferably more positive than 1.0 V vs SCE, as the above-described. When the dye is used in the black ink, the longer wavelength-absorbing dye (L) having a λmax in the region from 500 to 700 nm preferably has a half-value width of 100 nm or more in the absorption spectrum of a dilute solution standardized to an absorbance of 1.0, and also the shorter wavelength-absorbing dye (S) having a λmax in the region from 350 to 500 nm preferably has a broader half-value width.

As the shorter wavelength-absorbing dye (S) used in the above-described yellow, dark yellow and black ink, dyes of formulae (1), (3) and (4), particularly formulae (1) and (3) can be used.

Among dyes of formula (4), the azo dye of m=n=0 is preferred to the shorter wavelength-absorbing dye (2). In such a case, A and C each is preferably a heterocyclic group. the azo dye of m=n=1 is also preferred.

In any case, the oxidation potential (Eox) of the dye is preferably more positive than 1.0 V (vs SCE), and more preferably more positive than 1.2 V (vs SCE).

The content of each dye represented by formulae (1) to (7) in the inkjet ink is preferably from 0.2 to 20 mass%, more preferably from 0.5 to 15 mass% with respect to the entire ink. When two or more inks are used, the content of all of the inks preferably is included in the above range.

In the ink of the present invention, other dyes may be used in combination with the dyes of formulae (1) to (7) so as to obtain a full color image or adjust the color tone. Examples of the dye which can be used in combination include the followings.

Examples of the dye include, as the yellow dye, aryl- or heteryl-azo dyes having a phenol, a naphthol, an aniline, a pyrazolone, a pyridone or an open chain-type active methylene compound as the coupling component; azomethine dyes having an open chain-type active methylene compound as the coupling component; methine dyes such as benzylidene dye and monomethine oxonol dye; and quinone-base dyes such as naphthoquinone dye and anthraquinone dye. Other examples of the dye species include quinophthalone dye, nitro·nitroso dye, acridine dye and acridinone dye. These dyes may be a dye which provides a yellow color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure.

Examples of the dye include, as the magenta dye, aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; azomethine dyes having a pyrazolone or a pyrazolotriazole as the coupling component; methine dyes such as arylidene dye, styryl dye, merocyanine dye and oxonol dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; quinone-base dyes such as naphthoquinone, anthraquinone and anthrapyridone; and condensed polycyclic dyes such as dioxazine dye. These dyes may be a dye which

provides a magenta color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure.

Examples of the dye include, as the cyan dye, azomethine dyes such as indoaniline dye and indophenol dye; polymethine dyes such as cyanine dye, oxonol dye and merocyanine dye; carbonium dyes such as diphenylmethane dye, triphenylmethane dye and xanthene dye; phthalocyanine dyes; anthraquinone dyes; aryl- or heteryl-azo dyes having a phenol, a naphthol or an aniline as the coupling component; and indigo·thioindigo dyes. These dyes may be a dye which provides a cyan color for the first time when a part of the chromophore is dissociated. In this case, the counter cation may be an inorganic cation such as alkali metal and ammonium, an organic cation such as pyridinium and quaternary ammonium salt, or a polymer cation having such a cation in a partial structure.

In addition, a black dye such as polyazo dye may also be used.

Also, a water-soluble dye such as direct dye, acid dye, food dye, basic dye and reactive dye may be used in combination. Preferred examples thereof include the following dyes: C.I. Direct Red 2, 4, 9, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 21, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243 and 247; C.I. Direct Violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100 and 101; C.I. Direct Yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161 and 163; C.I. Direct Blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76, 77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 151, 156, 158, 159, 160, 168, 189, 192, 193, 194, 199, 200, 201, 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237, 244, 248, 249, 251, 252, 264, 270, 280, 288, 289 and 291; C.I. Direct Black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77, 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122, 125, 132, 146, 154, 166, 168, 173 and 199; C.I. Acid Red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 151, 154, 158, 249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396 and 397; C.I. Acid Violet 5, 34, 43, 47, 48, 90, 103 and 126; C.I. Acid Yellow 17, 19, 23, 25, 39, 40, 42, 44, 49, 50, 61, 64, 76, 79, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222 and 227; C.I. Acid Blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82, 92, 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205, 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277, 278, 279, 280, 288, 290 and 326; C.I. Acid Black 7, 24, 29, 48, 52:1 and 172; C.I. Reactive Red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49 and 55; C.I. Reactive Violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33 and 34; C.I. Reactive Yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41 and 42; C.I. Reactive Blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29 and 38; C.I. Reactive Black 4, 5, 8, 14, 21, 23, 26, 31, 32 and 34; C.I. Basic Red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45 and 46; C.I. Basic Violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40 and 48; C.I. Basic Yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39 and 40; C.I. Basic

Blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69 and 71; and C.I. Basic Black 8.

A pigment may be also used in combination.

As the pigment which can be used in the ink of the present invention, commercially available pigments and known pigments described in various publications can be used. Examples of the publication include Color Index, compiled by The Society of Dyers and Colourists, Kaitei Shin Han Ganryo Binran (Revised New Handbook of Pigments), compiled by Nippon Ganryo Gijutsu Kyokai (1989), Saishin Ganryo Oyo Gijutsu (Newest Pigment Application Technology), CMC Shuppan (1986), Insatsu Ink Gijutsu (Printing Ink Technique), CMC Shuppan (1984), and W. Herbst and K. Hunger, Industrial Organic Pigments, VCH Verlagsgesellschaft (1993). Specific examples of the pigment includes organic pigments such as azo pigments (e.g., azo lake pigment, insoluble azo pigment, condensed azo pigment, chelate azo pigment), polycyclic pigments (e.g., phthalocyanine-base pigment, anthraquinone-base pigment, perylene-base or perynone-base pigment, indigo-base pigment, quinacridone-base pigment, dioxazine-base pigment, isoindolinone-base pigment, quinophthalone-base pigment, diketopyrrolopyrrole-base pigment), dyeing lake pigments (lake pigments of acid or basic dye) and azine pigments, and inorganic pigments such as C.I. Pigment Yellow 34, 37, 42 and 53 which are a yellow pigment, C.I. Pigment Red 101 and 108 which are a red-type pigment, C.I. Pigment Blue 27, 29 and 17:1 which are a blue-type pigment, C.I. Pigment Black 7 and magnetite which are a black-type pigment, and C.I. Pigment White 4, 6, 18 and 21 which are a white-type pigment.

The pigment having a color tone preferred for the formation of an image includes the followings. As the blue to cyan pigment, phthalocyanine pigments, anthraquinone-type indanthrone pigments (for example, C.I. Pigment Blue 60) and dyeing lake pigment-type triarylcarbonium pigments are preferred, and phthalocyanine pigments are most preferred (preferred examples thereof include copper phthalocyanine such as C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4 and 15:6, monochloro or low chlorinated copper phthalocyanine, aluminum phthalocyanine such as pigments described in European Patent 860475, nonmetallic phthalocyanine such as C.I. Pigment Blue 16, and phthalocyanine with the center metal being Zn, Ni or Ti, and among these, C.I. Pigment Blue 15:3 and 15:4 and aluminum phthalocyanine are more preferred).

As the red to violet pigment, azo pigments (preferred examples thereof include C.I. Pigment Red 3, 5, 11, 22, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 52:1, 53:1, 57:1, 63:2, 144, 146 and 184, and among these, C.I. Pigment Red 57:1, 146 and 184 are more preferred), quinacridone-base pigments (preferred examples thereof include C.I. Pigment Red 122, 192, 202, 207 and 209 and C.I. Pigment Violet 19 and 42, and among these, C.I. Pigment Red 122 is more preferred), dyeing lake pigment-type triarylcarbonium pigments (preferred examples thereof include xanthene-base C.I. Pigment Red 81:1 and C.I. Pigment Violet 1, 2, 3, 27 and 39), dioxazine-base pigments (for example, C.I. Pigment Violet 23 and 37), diketopyrrolopyrrole-base pigments (for example, C.I. Pigment Red 254), perylene

pigments (for example, C.I. Pigment Violet 29), anthraquinone-base pigments (for example, C.I. Pigment Violet 5:1, 31 and 33) and thioindigo-base pigments (for example, C.I. Pigment Red 38 and 88) are preferred.

As the yellow pigment, azo pigments (preferred examples thereof include monoazo pigment-type C.I. Pigment Yellow 1, 3, 74 and 98, disazo pigment-type C.I. Pigment Yellow 12, 13, 14, 16, 17 and 83, synthetic azo-base C.I. Pigment Yellow 93, 94, 95, 128 and 155, and benzimidazolone-base C.I. Pigment Yellow 120, 151, 154, 156 and 180, and among these, those not using a benzidine-base compound as a raw material are more preferred), isoindoline·isoindolinone-base pigments (preferred examples thereof include C.I. Pigment Yellow 109, 110, 137 and 139), quinophthalone pigments (preferred examples thereof include C.I. Pigment Yellow 138) and flavanthrone pigments (for example, C.I. Pigment Yellow 24) are preferred.

As the black pigment, inorganic pigments (preferred examples thereof include carbon black and magnetite) and aniline black are preferred.

Other than these, an orange pigment (for example, C.I. Pigment Orange 13 and 16) and a green pigment (for example, C.I. Pigment Green 7) may be used.

The components of the ink used in the ink set of the invention, other than the dye or pigment, are described below.

The surfactant which can be contained in the inkjet ink of the present invention is described below.

In the present invention, a surfactant may be incorporated into the inkjet ink to control the liquid properties of ink, whereby excellent effects can be provided, such as enhancement of ejection stability of the ink, improvement of water resistance of the image and prevention of bleeding of the printed ink.

Examples of the surfactant include anionic surfactants such as sodium dodecylsulfate, sodium dodecyloxysulfonate and sodium alkylbenzenesulfonate, cationic surfactants such as cetylpyridinium chloride, trimethylcetylammonium chloride and tetrabutylammonium chloride, and nonionic surfactants such as polyoxyethylene nonylphenyl ether, polyoxyethylene naphthyl ether and polyoxyethylene octylphenyl ether. Among these, nonionic surfactants are preferred.

The surfactant content is from 0.001 to 15 mass%, preferably from 0.005 to 10 mass%, more preferably from 0.01 to 5 mass%, based on the ink.

The inkjet ink of the present invention can be prepared by dissolving or dispersing the above-described dye and preferably the surfactant in an aqueous medium. The term "aqueous medium" as used in the present invention means water or a mixture of water and a slight amount of water-miscible organic solvent, where additives such as wetting agent, stabilizer and antiseptic are added, if desired.

In preparing the ink solution of the present invention, in the case of a water-soluble ink, the

dye is preferably first dissolved in water and thereafter, various solvents and additives are added, dissolved and mixed to provide a uniform ink solution.

For dissolving the dye and the like, various methods such as stirring, ultrasonic irradiation and shaking can be used. Among these, stirring is preferred. In performing the stirring, various systems known in this field can be used, such as flow stirring and stirring utilizing the shearing force by means of a reversal agitator or a dissolver. Also, a stirring method utilizing the shearing force with the bottom surface of a container, such as magnetic stirrer, can be advantageously used.

Examples of the water-miscible organic solvent which can be used in the present invention include alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, tert-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol), polyhydric alcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentanediol, glycerin, hexanetriol, thiodiglycol), glycol derivatives (e.g., ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl ether, ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyethyleneimine, tetramethylpropylenediamine) and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, 2-pyrrolidone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 2-oxazolidone, 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone). These water-miscible organic solvents can be used in combination of two or more thereof.

In the case where the above-described dye is an oil-soluble dye, the ink solution can be prepared by dissolving the oil-soluble dye in a high boiling point organic solvent and emulsion-dispersing it in an aqueous medium.

The high boiling point organic solvent for use in the present invention has a boiling point of 150°C or more, preferably 170°C or more.

Examples thereof include phthalic acid esters (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl) isophthalate, bis(1,1-diethylpropyl) phthalate), esters of phosphoric acid or phosphone (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, dioctylbutyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, di-2-ethylhexylphenyl phosphate), benzoic acid esters (e.g., 2-ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl benzoate, 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecanamide, N,N-

diethyllaurylamide), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-tert-amylphenol), aliphatic esters (e.g., dibutoxyethyl succinate, di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanoate, tributyl citrate, diethyl azelate, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins (e.g., paraffins having a chlorine content of 10 to 80%), trimesic acid esters (e.g., tributyl trimesate), dodecylbenzene, diisopropylnaphthalene, phenols (e.g., 2,4-di-tert-amylphenol, 4-dodecyloxyphenol, 4-dodecyloxycarbonylphenol, 4-(4-dodecyloxyphenylsulfonyl)phenol), carboxylic acids (e.g., 2-(2,4-di-tert-amylphenoxy)butyric acid, 2-ethoxyoctanedecanoic acid) and alkylphosphoric acids (e.g., di-(2-ethylhexyl)phosphoric acid, diphenylphosphoric acid). The high boiling point organic solvent can be used in an amount of, in terms of the mass ratio to the oil-soluble dye, from 0.01 to 3 times, preferably from 0.01 to 1.0 times.

These high boiling point organic solvents may be used individually or as a mixture of several kinds [for example, tricresyl phosphate and dibutyl phthalate, trioctyl phosphate and di(2-ethylhexyl) sebacate, or dibutyl phthalate and poly(N-tert-butylacrylamide)].

Examples of the high boiling point organic solvent for use in the present invention, other than the above-described compounds, and/or the synthesis method of these high boiling point organic solvents are described, for example, in U.S. Patents 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,928, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,430,422, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599, 4,745,049, 4,935,321 and 5,013,639, EP-A-276319, EP-A-286253, EP-A-289820, EP-A-309158, EP-A-309159, EP-A-309160, EP-A-509311, EP-A-510576, East German Patents 147009, 157147, 159573 and 225240A, British Patent 2091124A, JP-A-48-47335, JP-A-50-26530, JP-A-51-25133, JP-A-51-26036, JP-A-51-27921, JP-A-51-27922, JP-A-51-149028, JP-A-52-46816, JP-A-53-1520, JP-A-53-1521, JP-A-53-15127, JP-A-53-146622, JP-A-54-91325, JP-A-54-106228, JP-A-54-118246, JP-A-55-59464, JP-A-56-64333, JP-A-56-81836, JP-A-59-204041, JP-A-61-84641, JP-A-62-118345, JP-A-62-247364, JP-A-63-167357, JP-A-63-214744, JP-A-63-301941, JP-A-64-9452, JP-A-64-9454, JP-A-64-68745, JP-A-1-101543, JP-A-1-102454, JP-A-2-792, JP-A-2-4239, JP-A-2-43541, JP-A-4-29237, JP-A-4-30165, JP-A-4-232946 and JP-A-4-346338.

The high boiling point organic solvent is used in an amount of, in terms of the mass ratio to the oil-soluble dye, from 0.01 to 3.0 times, preferably from 0.01 to 1.0 times.

In the present invention, the oil-soluble dye or high boiling point organic solvent is used by emulsion-dispersing it in an aqueous medium. Depending on the case, a low boiling point organic solvent may also be used at the emulsion-dispersion in view of emulsifiability. The low boiling point organic solvent is an organic solvent having a boiling point of about 30 to 150°C at atmospheric pressure. Preferred examples thereof include esters (e.g., ethyl acetate, butyl acetate, ethyl propionate, β-ethoxyethyl acetate, methylcellosolve acetate), alcohols (e.g., isopropyl alcohol, n-butyl

alcohol, secondary butyl alcohol), ketones (e.g., methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone), amides (e.g., dimethylformamide, N-methylpyrrolidone) and ethers (e.g., tetrahydrofuran, dioxane), however, the present invention is not limited thereto.

In the emulsion-dispersion, an oil phase obtained by dissolving the dye in a high boiling organic solvent or depending on the case, in a mixed solvent of a high boiling organic solvent and a low boiling organic solvent is dispersed in an aqueous phase mainly comprising water to form fine oil droplets of the oil phase. At this time, in either one or both of the aqueous phase and the oil phase, additives described later, such as surfactant, wetting agent, dye stabilizer, emulsification stabilizer, antiseptic and fungicide, can be added, if desired.

In the general emulsification method, an oil phase is added to an aqueous phase, however, a so-called phase inversion emulsification method of adding dropwise an aqueous phase in an oil phase can also be preferably used. The above-described emulsification method can be applied also when the dye used in the present invention is water-soluble and the additives are oil-soluble.

In performing the emulsion-dispersion, various surfactants can be used. Preferred examples thereof include anionic surfactants such as fatty acid salt, alkylsulfuric ester salt, alkylbenzenesulfonate, alkylnaphthalenesulfonate, dialkylsulfosuccinate, alkylphosphoric ester salt, naphthalenesulfonic acid formalin condensate and polyoxyethylene alkylsulfuric ester salt, and nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine, glycerin fatty acid ester and oxyethylene oxypropylene block copolymer. Also, SURFYNOLS (produced by Air Products & Chemicals), which are an acetylene-base polyoxyethylene oxide surfactant, are preferably used. Furthermore, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. In addition, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can also be used.

For the purpose of stabilizing the dispersion immediately after the emulsification, a water-soluble polymer may be added in combination with the surfactant. Preferred examples of the water-soluble polymer include polyvinyl alcohol, polyvinylpyrrolidone, polyethylene oxide, polyacrylic acid, polyacrylamide and copolymers thereof. Other than these, natural water-soluble polymers such as polysaccharides, casein and gelatin are also preferably used. Furthermore, for the stabilization of the dye dispersion, a polymer which does not substantially dissolve in an aqueous medium, such as polyvinyl, polyurethane, polyester, polyamide, polyurea and polycarbonate obtained by the polymerization of acrylic acid esters, methacrylic acid esters, vinyl esters, acrylamides, methacrylamides, olefins, styrenes, vinyl ethers or acrylonitriles, can also be used in combination. This polymer preferably contains $-SO_3^-$ or $-COO^-$. In the case of using this polymer which does not substantially dissolve in an aqueous medium, the polymer is preferably used in an amount of 20

mass% or less, more preferably 10 mass% or less, based on the high boiling point organic solvent.

In preparing an aqueous ink composition by dispersing the oil-soluble dye or high boiling point organic solvent according to emulsion-dispersion, control of the particle size is important. In order to elevate the color purity or density of an image formed by the inkjet recording, it is essential to reduce the average particle size. The average particle size is, in terms of the volume average particle size, preferably 1 μm or less, more preferably from 5 to 100 nm.

The volume average particle size and particle size distribution of the dispersed particles can be easily measured by a known method such as static light scattering method, dynamic light scattering method, centrifugal precipitation method and the method described in Jikken Kagaku Koza (Lecture of Experimental Chemistry), 4th ed., pp. 417-418. For example, the ink is diluted with distilled water to have a particle concentration of 0.1 to 1 mass%, then, the particle size can be easily measured by a commercially available volume average particle size measuring apparatus (for example, Microtrac UPA, manufactured by Nikkiso K.K.). The dynamic light scattering method utilizing the laser Doppler effect is particularly preferred because even a small particle size can be measured.

The volume average particle size is an average particle size weighted with the particle volume and is obtained by multiplying the diameter of individual particles in the gathering of particles with the volume of the particle and dividing the sum total of the obtained values by the total volume of the particles. The volume average particle size is described in Soichi Muroi, Kobunshi Latex no Kagaku (Chemistry of Polymer Latex), page 119, Kobunshi Kanko Kai.

Also, it is revealed that the presence of coarse particles greatly affects the printing performance. More specifically, the coarse particle clogs the nozzle of head or even if the nozzle is not clogged, forms a soil to bring about failure or slippage in the ejection of ink and this seriously affects the printing performance. In order to prevent these troubles, it is important to reduce the number of particles having a particle size of 5 μm or more to 10 or less and the number of particles having a particle size of 1 μm or more to 1,000 or less, in 1 μl of ink prepared.

For removing these coarse particles, a known method such as centrifugal separation or microfiltration can be used. This separation step may be performed immediately after the emulsion-dispersion or may be performed immediately before filling the ink in an ink cartridge after various additives such as wetting agent and surfactant are added to the emulsified dispersion.

A mechanically emulsifying apparatus is effective for reducing the average particle size and eliminating coarse particles.

As for the emulsifying apparatus, known apparatuses such as simple stirrer, impeller stirring system, in-line stirring system, mill system (e.g., colloid mill) and ultrasonic system can be used, however, a high-pressure homogenizer is particularly preferred.

The mechanism of the high-pressure homogenizer is described in detail in U.S. Patent 4,533,254 and JP-A-6-47264. Examples of the commercially available apparatus include Gaulin

Homogenizer (manufactured by A.P. V Gaulin Inc.), Microfluidizer (manufactured by Microfluidex Inc.) and Altimizer (produced by Sugino Machine).

The high-pressure homogenizer with a mechanism of pulverizing particles in an ultrahigh pressure jet stream recently described in U.S. Patent 5,720,551 is particularly effective for the emulsion-dispersion of the present invention. Examples of the emulsifying apparatus using this ultrahigh pressure jet stream include DeBEE2000 (manufactured by BEE International Ltd.).

In performing the emulsification by a high-pressure emulsion-dispersing apparatus, the pressure is 50 MPa or more, preferably 60 MPa or more, more preferably 180 MPa or more.

A method of using two or more emulsifying apparatuses, for example, by performing the emulsification in a stirring emulsifier and then passing the emulsified product through a high-pressure homogenizer is particularly preferred. Also, a method of once performing the emulsion-dispersion by such an emulsifying apparatus and after adding additives such as wetting agent and surfactant, again passing the dispersion through a high-pressure homogenizer during the time of filling the ink into a cartridge is preferred.

In the case of containing a low boiling point organic solvent in addition to the high boiling point organic solvent, the low boiling point solvent is preferably removed in view of stability of the emulsified product, safety and hygiene. For removing the low boiling point solvent, various known methods can be used according to the kind of the solvent. Examples of the method include evaporation, vacuum evaporation and ultrafiltration. This removal of the low boiling point organic solvent is preferably performed as soon as possible immediately after the emulsification.

The preparation method of the inkjet ink is described in detail in JP-A-5-148436, JP-A-5-295312, JP-A-7-97541, JP-A-7-82515 and JP-A-7-118584 and the methods described in these patent publications can be utilized also in the preparation of the ink for inkjet recording of the present invention.

In the inkjet ink of the present invention, additives such as drying inhibitor for preventing clogging due to drying of ink at the ejection port, permeation accelerator for attaining more successful permeation of ink into paper, ultraviolet absorbent, antioxidant, viscosity adjusting agent, surface tension adjusting agent, dispersant, dispersion stabilizer, fungicide, rust inhibitor, pH adjusting agent, defoaming agent and chelating agent, can be appropriately selected and used in an appropriate amount.

The drying inhibitor for use in the present invention is preferably a water-soluble organic solvent having a vapor pressure lower than water. Specific examples thereof include polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, polyethylene glycol, thiodiglycol, dithiodiglycol, 2-methyl-1,3-propanediol, 1,2,6-hexanetriol, acetylene glycol derivative, glycerin and trimethylolpropane; lower alkyl ethers of polyhydric alcohol, such as ethylene glycol monomethyl(or ethyl) ether, diethylene glycol monomethyl(or ethyl) ether and triethylene glycol monoethyl(or butyl) ether; heterocyclic rings such as 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-

dimethyl-2-imidazolidinone and N-ethylmorpholine; sulfur-containing compounds such as sulfolane, dimethylsulfoxide and 3-sulfolene; polyfunctional compounds such as diacetone alcohol and diethanolamine; and urea derivatives. Among these, polyhydric alcohols such as glycerin and diethylene glycol are preferred. These drying inhibitors may be used individually or in combination of two or more thereof. The drying inhibitor is preferably contained in an amount of 10 to 50 mass% in the ink.

Examples of the permeation accelerator which can be used in the present invention include alcohols such as ethanol, isopropanol, butanol, di(tri)ethylene glycol monobutyl ether and 1,2-hexanediol, sodium laurylsulfate, sodium oleate and nonionic surfactants. A sufficiently high effect can be obtained by adding from 10 to 30 mass% of the permeation accelerator in the ink. The permeation accelerator is preferably used in an amount of causing no blurring of printed letter or no print through.

Examples of the ultraviolet absorbent which can be used in the present invention for improving the preservability of image include benzotriazole-base compounds described in JP-A-58-185677, JP-A-61-190537, JP-A-2-782, JP-A-5-197075 and JP-A-9-34057, benzophenone-base compounds described in JP-A-46-2784, JP-A-5-194483 and U.S. Patent 3,214,463, cinnamic acid-base compounds described in JP-B-48-30492 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-B-56-21141 and JP-A-10-88106, triazine-base compounds described in JP-A-4-298503, JP-A-8-53427, JP-A-8-239368, JP-A-10-182621 and JP-T-8-501291 (the term "JP-T" as used herein means a "published Japanese translation of a PCT patent application"), compounds described in Research Disclosure No. 24239, and compounds of absorbing ultraviolet light and emitting fluorescent light, so-called fluorescent brightening agents, represented by stilbene-base compounds and benzoxazole-base compounds.

As the antioxidant which can be used in the present invention for improving the preservability of image, various organic or metal complex-base discoloration inhibitors can be used. Examples of the organic discoloration inhibitor include hydroquinones, alkoxyphenols, dialkoxyphenols, phenols, anilines, amines, indanes, chromans, alkoxyanilines and heterocyclic rings. Examples of the metal complex include nickel complex and zinc complex. More specifically, compounds described in patents cited in Research Disclosure, Nos. 17643 (Items VII-I to VII-J), 15162, 18716 (page 650, left column), 36544 (page 527), 307105 (page 872) and 15162, and compounds included in formulae of representative compounds and in exemplary compounds described in JP-A-62-215272 (pages 127 to 137) can be used.

Examples of the fungicide for use in the present invention include sodium dehydroacetate, sodium benzoate, sodium pyridinethione-1-oxide, ethyl p-hydroxybenzoate, 1,2-benzisothiazolin-3-one and salts thereof. The fungicide is preferably used in an amount of 0.02 to 5.00 mass% in the ink.

The fungicide is described in detail in Bokin Bobai Zai Jiten (Dictionary of Microbicide and Fungicide), compiled by Nippon Bokin Bobai Gakkai Jiten Henshu Iinkai.

Examples of the rust inhibitor include acidic sulfite, sodium thiosulfate, ammon thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite and benzotriazole. The rust inhibitor is preferably used in an amount of 0.02 to 5.00 mass% in the ink.

The pH adjusting agent for use in the present invention can be suitably used for adjusting the pH and imparting dispersion stability. The pH of the ink is preferably adjusted to 4 to 11 at 25°C. If the pH is less than 4, the solubility of dye decreases to readily cause clogging of a nozzle, whereas if it exceeds 11, the water resistance is liable to deteriorate. Examples of the pH adjusting agent include basic compounds such as organic base and inorganic alkali, and acidic compounds such as organic acid and inorganic acid.

As the basic compound, inorganic compounds such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium acetate, potassium acetate, sodium phosphate and sodium monohydrogenphosphate, and organic bases such as aqueous ammonia, methylamine, ethylamine, diethylamine, triethylamine, ethanolamine, diethanolamine, triethanolamine, ethylenediamine, piperidine, diazabicyclooctane, diazabicycloundecene, pyridine, quinoline, picoline, lutidine and collidine, can also be used.

As the acidic compound, inorganic compounds such as hydrochloric acid, sulfuric acid, phosphoric acid, boric acid, sodium hydrogensulfate, potassium hydrogensulfate, potassium dihydrogenphosphate and sodium dihydrogenphosphate, and organic compounds such as acetic acid, tartaric acid, benzoic acid, trifluoroacetic acid, methanesulfonic acid, ethanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, saccharinic acid, phthalic acid, picolinic acid and quinolinic acid, can also be used.

The ink of the present invention preferably has a conductivity of 0.01 to 10 S/m, more preferably from 0.05 to 5 S/m.

The conductivity can be measured by an electrode method using a commercially available saturated potassium chloride.

The conductivity can be controlled mainly by the ion concentration in an aqueous solution. In the case where the salt concentration is high, desalting can be performed by using ultrafiltration membrane or the like. Also, in the case of controlling the conductivity by adding a salt or the like, the conductivity can be controlled by adding various organic or inorganic salts.

Examples of the inorganic salt which can be used include inorganic compounds such as potassium halide, sodium halide, sodium sulfate, potassium sulfate, sodium hydrogensulfate, potassium hydrogensulfate, sodium nitrate, potassium nitrate, sodium hydrogencarbonate, potassium

hydrogencarbonate, sodium phosphate, sodium monohydrogenphosphate, boric acid, potassium dihydrogenphosphate and sodium dihydrogenphosphate. Also, organic compounds such as sodium acetate, potassium acetate, potassium tartrate, sodium tartrate, sodium benzoate, potassium benzoate, sodium p-toluenesulfonate, potassium saccharinate, potassium phthalate and sodium picolinate can be used.

The conductivity can also be controlled by selecting the component of other additives.

The ink of the present invention has a viscosity at 25°C of 1 to 20 mPa·s, preferably from 2 to 15 mPa·s, more preferably from 2 to 10 mPa·s. If the viscosity exceeds 30 mPa·s, the fixing rate of the recorded image decreases and the ejection performance also decreases, whereas if it is less than 1 mPa·s, the recorded image is blurred to decrease the grade.

The viscosity can be freely adjusted by the amount of the ink solvent added. Examples of the ink solvent include glycerin, diethylene glycol, triethanolamine, 2-pyrrolidone, diethylene glycol monobutyl ether and triethylene glycol monobutyl ether.

A viscosity adjusting agent may also be used. Examples of the viscosity adjusting agent include water-soluble polymers such as celluloses and polyvinyl alcohol, and nonionic surfactants. The viscosity adjusting agent is described in detail in <u>Nendo Chosei Gijutsu (Viscosity Adjusting Technology)</u>, Chap. 9, Gijutsu Joho Kyokai (1999), and <u>Inkjet Printer Yo Chemicals (98 Zoho) - Zairyo no Kaihatsu Doko·Tenbo Chosa- (Chemicals for Inkjet Printer (Enlarged Edition of 98) - Survey on Tendency· Prospect of Development of Materials-)</u>, pp. 162-174, CMC (1997).

The method for measuring the viscosity of liquid is described in detail in JIS Z8803 but the viscosity can be simply and easily measured by a commercially available viscometer and examples of the rotational viscometer include B-type viscometer and E-type viscometer manufactured by Tokyo Keiki Co. In the present invention, the viscosity is measured at 25°C by using a vibrating viscometer Model VM-100A-L manufactured by Yamaichi Denki. The unit of viscosity is pascal second (Pa·s) but usually, milli-pascal second (mPa·s) is used.

The surface tension of the ink for use in the present invention is, irrespective of dynamic surface tension or static surface tension, preferably from 20 to 50 mN/m, more preferably from 20 to 40 mN/m, at 25°C. If the surface tension exceeds 50 mN/m, ejection stability and printing quality are seriously deteriorated, for example, bleeding at color mixing or feathering is caused, whereas if the surface tension of the ink is less than 20 mN/m, printing failure may occur due to, for example, attachment of ink to the hard surface at the ejection.

For the purpose of adjusting the surface tension, a cationic, anionic or nonionic surfactant of various types can be added. The surfactant is preferably used in the range from 0.01 to 20 mass%, more preferably from 0.1 to 10 mass%, based on the inkjet ink. The surfactants can be used in combination of two or more thereof.

As the method for measuring the static surface tension, a capillary elevation method, a

dropping method, a suspended ring method and the like are known. In the present invention, a vertical plate method is used as the method for measuring the static surface tension.

When a glass or platinum thin plate is vertically suspended while dipping a part of the plate in a liquid, a surface tension of the liquid acts downward along the portion of contact between the liquid surface and the plate. This force is balanced by an upward force and thereby, the surface tension can be measured.

As the method for measuring the dynamic surface tension, a vibrating jet method, a meniscus dropping method, a maximum bubble pressure method and the like are known and these are described, for example, in Shin Jikken Kagaku Koza, Kaimen to Colloid (New Lecture of Experimental Chemistry, Interface and Colloid), Vol. 18, pp. 69-90, Maruzen (1977). Furthermore, a liquid film rupturing method described in JP-A-3-2064 is known. In the present invention, a differential bubble pressure method is used as the method for measuring the dynamic surface tension. The principle and method of this measurement are described below.

When a bubble is generated in a solution rendered uniform by stirring, a gas-liquid interface is newly produced and surfactant molecules in the solution gather to the water surface at a constant speed. When the bubble rate (bubble generation rate) is changed, as the generation rate decreases, a larger number of surfactant molecules gather to the bubble surface. Therefore, the maximum bubble pressure immediately before the bubble bursts becomes small and the maximum bubble pressure (surface tension) for the bubble rate can be detected. The dynamic surface tension is preferably measured by a method of generating a bubble in a solution by using large and small two probes, measuring the differential pressure between two probes in the maximum bubble pressure state, and calculating the dynamic surface tension.

In view of ejection stability of ink, quality of printed image, various fastnesses of image and reduction in blurring of image after printing or in stickiness on the printed surface, the content of the nonvolatile component in the ink of the present invention is preferably from 10 to 70 mass% based on the entire amount of the ink. In view of ejection stability of ink and reduction in blurring of image after printing, the content of the nonvolatile component is more preferably from 20 to 60 mass%.

The nonvolatile component as used herein means a liquid or solid component having a boiling point of 150°C or more at 1 atm or a high molecular weight component. The nonvolatile component in the ink for inkjet ink recording includes a dye and a high boiling point solvent and also includes a polymer latex, a surfactant, a dye stabilizer, a fungicide and a buffering agent which are added, if desired. Many of these nonvolatile components except for the dye stabilizer reduce the dispersion stability of ink and even after printing, remain on the inkjet image-receiving paper to inhibit the aggregation and in turn stabilization of dye on the image-receiving paper and worsen various fastnesses of the image area or blurring of the image under high humidity condition.

In the present invention, a high molecular weight compound may also be contained. The

high molecular weight compound as used herein indicates all polymer compounds having a number average molecular weight of 5,000 or more contained in the ink. Examples of the polymer compound include a water-soluble polymer compound which substantially dissolves in an aqueous medium, a water-dispersible polymer compound such as polymer latex and polymer emulsion, and an alcohol-soluble polymer compound which dissolves in a polyhydric alcohol used as an auxiliary solvent, however, the high molecular weight compound as used in the present invention includes any polymer compound if it substantially dissolves or disperses uniformly in the ink solution.

Specific examples of the water-soluble polymer compound include water-soluble polymers such as polyvinyl alcohol, silanol-modified polyvinyl alcohol, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinylpyrrolidone, polyalkylene oxide (e.g., polyethylene oxide, polypropylene oxide) and polyalkylene oxide derivatives; natural water-soluble polymers such as polysaccharides, starch, cationized starch, casein and gelatin; aqueous acrylic resins such as polyacrylic acid, polyacrylamide and copolymers thereof; aqueous alkyd resin; and water-soluble polymer compounds having a $-SO_3^-$ or $-COO^-$ group within the molecule and substantially dissolvable in an aqueous medium.

Specific examples of the polymer latex include a styrene-butadiene latex, a styrene-acryl latex and a polyurethane latex, and specific examples of the polymer emulsion include an acryl emulsion.

These water-soluble polymer compounds can be used individually or in combination of two or more thereof.

As described above, the water-soluble polymer compound is used as the viscosity adjusting agent so as to adjust the viscosity of ink to a viscosity region of giving good ejection property, however, if the amount of the water-soluble polymer compound added is large, the viscosity of ink increases to reduce the ejection stability of ink solution and after aging of ink, the nozzle is readily clogged by the precipitate.

The amount added of the polymer compound as the viscosity adjusting agent varies depending on the molecular weight of the compound added (as the molecular weight is higher, the amount added can be smaller), but the amount added is from 0 to 5 mass%, preferably from 0 to 3 mass%, more preferably from 0 to 1 mass%, based on the entire amount of ink.

In the present invention, apart from the above-described surfactants, a nonionic, cationic or anionic surfactant is used as the surface tension adjusting agent. Examples of the anionic surfactant include a fatty acid salt, an alkylsulfuric ester salt, an alkylbenzenesulfonate, an alkylnaphthalenesulfonate, a dialkylsulfosuccinate, an alkylphosphoric ester salt, a naphthalenesulfonic acid formalin condensate and a polyoxyethylenealkylsulfuric ester salt. Examples of the nonionic surfactant include a polyoxyethylene alkyl ether, a polyoxyethylene alkylallyl ether, a polyoxyethylene fatty acid ester, a sorbitan fatty acid ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene alkylamine, a glycerin fatty acid ester and an oxyethylene

oxypropylene block copolymer. Also, SURFYNOLS (produced by Air Products & Chemicals), which are an acetylene-base polyoxyethylene oxide surfactant, are preferably used. Furthermore, amine oxide-type amphoteric surfactants such as N,N-dimethyl-N-alkylamine oxide are preferred. In addition, surfactants described in JP-A-59-157636 (pages (37) to (38)) and Research Disclosure, No. 308119 (1989) can be used.

The surface tension of the ink for use in the present invention is preferably from 20 to 60 mN/m, more preferably from 25 to 45 mN/m with or without use of the above compound.

In the present invention, if desired, various cationic, anionic or nonionic surfactants described above may be used as a dispersant or a dispersion stabilizer, and fluorine- or silicone-base compounds or chelating agents represented by EDTA may be used as a defoaming agent.

The image-receiving material for use in the present invention includes recording paper and recording film described below, which are a reflective medium.

The support which can be used for the recording paper or film is produced, for example, from a chemical pulp such as LBKP and NBKP, a mechanical pulp such as GP, PGW, RMP, TMP, CTMP, CMP and CGP, or a waste paper pulp such as DIP, by mixing, if desired, conventionally known additives such as pigment, binder, sizing agent, fixing agent, cation agent and paper strength increasing agent, and then sheeting the mixture by using various devices such as Fourdrinier paper machine and cylinder paper machine. Other than these supports, synthetic paper or plastic film may be used. The thickness of the support is preferably from 10 to 250 μm and the basis weight is preferably from 10 to 250 g/m^2.

An image-receiving layer and a backcoat layer may be provided on the support as it is to produce an image-receiving material for the ink of the present invention, or after providing a size press or anchor coat layer by using starch, polyvinyl alcohol or the like, an image-receiving layer and a backcoat layer may be provided to produce an image-receiving material. The support may be further subjected to a flattening treatment by a calendering device such as machine calender, TG calender and soft calender.

In the present invention, the support is preferably paper or plastic film of which both surfaces are laminated with polyolefin (for example, polyethylene, polystyrene, polybutene or a copolymer thereof) or polyethylene terephthalate. In the polyolefin, a white pigment (for example, titanium oxide or zinc oxide) or a tinting dye (for example, cobalt blue, ultramarine or neodymium oxide) is preferably added.

The image-receiving layer provided on the support contains a porous material and an aqueous binder. Also, the image-receiving layer preferably contains a pigment and the pigment is preferably a white pigment. Examples of the white pigment include inorganic white pigments such as calcium carbonate, kaolin, talc, clay, diatomaceous earth, synthetic amorphous silica, aluminum silicate, magnesium silicate, calcium silicate, aluminum hydroxide, alumina, lithopone, zeolite,

barium sulfate, calcium sulfate, titanium dioxide, zinc sulfide and zinc carbonate, and organic pigments such as styrene-base pigment, acryl-base pigment, urea resin and melamine resin. Among these, porous inorganic white pigments are preferred, and synthetic amorphous silica and the like having a large pore area are more preferred. The synthetic amorphous silica may be either a silicic acid anhydride obtained by a dry production method (gas phase method) or a silicic acid hydrate obtained by a wet production method.

Specific examples of the recording paper containing the pigment in the image-receiving layer include those disclosed in JP-A-10-81064, JP-A-10-119423, JP-A-10-157277, JP-A-10-217601, JP-A-11-348409, JP-A-2001-138621, JP-A-2000-43401, JP-A-2000-211235, JP-A-2000-309157, JP-A-2001-96897, JP-A-2001-138627, JP-A-11-91242, JP-A-8-2087, JP-A-8-2090, JP-A-8-2091, JP-A-8-2093, JP-A-8-174992, JP-A-11-192777 and JP-A-2001-301314.

Examples of the aqueous binder contained in the image-receiving layer include water-soluble polymers such as polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinylpyrrolidone, polyalkylene oxide and polyalkylene oxide derivatives, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. These aqueous binders can be used individually or in combination of two or more thereof. Among these, polyvinyl alcohol and silanol-modified polyvinyl alcohol are preferred in the present invention in view of adhesion to the pigment and peeling resistance of the ink-receiving layer.

The image-receiving layer may contain a mordant, a water-proofing agent, a light fastness enhancer, a gas resistance enhancer, a surfactant, a hardening agent and other additives in addition to the pigment and the aqueous binder.

The mordant added to the image-receiving layer is preferably immobilized and for this purpose, a polymer mordant is preferably used.

The polymer mordant is described in JP-A-48-28325, JP-A-54-74430, JP-A-54-124726, JP-A-55-22766, JP-A-55-142339, JP-A-60-23850, JP-A-60-23851, JP-A-60-23852, JP-A-60-23853, JP-A-60-57836, JP-A-60-60643, JP-A-60-118834, JP-A-60-122940, JP-A-60-122941, JP-A-60-122942, JP-A-60-235134, JP-A-1-161236 and U.S. Patents 2,484,430, 2,548,564, 3,148,061, 3,309,690, 4,115,124, 4,124,386, 4,193,800, 4,273,853, 4,282,305 and 4,450,224. An image-receiving material containing the polymer mordant described in JP-A-1-161236 (pages 212 to 215) is particularly preferred. When the polymer mordant described in this patent publication is used, an image having excellent image quality can be obtained and at the same time, the light fastness of the image is improved.

The water-proofing agent is effective for obtaining a water-resistant image. The water-proofing agent is preferably a cationic resin. Examples of the cationic resin include polyamidopolyamine epichlorohydrin, polyethyleneimine, polyaminesulfone, poly-dimethyldiallyl-

ammonium chloride and cation polyacrylamide. The content of the cationic resin is preferably from 1 to 15 mass%, more preferably from 3 to 10 mass%, based on the entire solid content of the ink-receiving layer.

Examples of the light fastness enhancer and the gas resistance enhancer include phenol compounds, hindered phenol compounds, thioether compounds, thiourea compounds, thiocyanic acid compounds, amine compounds, hindered amine compounds, TEMPO compounds, hydrazine compounds, hydrazide compounds, amidine compounds, vinyl group-containing compounds, ester compounds, amide compounds, ether compounds, alcohol compounds, sulfinic acid compounds, saccharides, water-soluble reducing compounds, organic acids, inorganic acids, hydroxy group-containing organic acids, benzotriazole compounds, benzophenone compounds, triazine compounds, heterocyclic compounds, water-soluble metal salts, organic metal compounds and metal complexes.

Specific examples of these compounds include those described in JP-A-10-182621, JP-A-2001-260519, JP-A-2000-260519, JP-B-4-34953, JP-B-4-34513, JP-B-4-34512, JP-A-11-170686, JP-A-60-67190, JP-A-7-276808, JP-A-2000-94829, JP-T-8-512258 and JP-A-11-321090.

The surfactant functions as a coating aid, a releasability improver, a slipperiness improver or an antistatic agent. The surfactant is described in JP-A-62-173463 and JP-A-62-183457.

In place of the surfactant, an organic fluoro compound may be used. The organic fluoro compound is preferably hydrophobic. Examples of the organic fluoro compound include fluorine-containing surfactants, oily fluorine-base compounds (for example, fluorine oil) and solid fluorine compound resins (for example, ethylene tetrafluoride resin). The organic fluoro compound is described in JP-B-57-9053 (columns 8 to 17), JP-A-61-20994 and JP-A-62-135826.

As the hardening agent, for example, the materials described in JP-A-1-161236 (page 222), JP-A-9-263036, JP-A-10-119423 and JP-A-2001-310547 can be used.

Other examples of the additive added to the image-receiving layer include a pigment dispersant, a thickener, a defoaming agent, a dye, a fluorescent brightening agent, an antiseptic, a pH adjusting agent, a matting agent and a hardening agent. The ink-receiving layer may be composed of one layer or two layers.

In the recording paper or film, a backcoat layer may also be provided. Examples of the component which can be added to this layer include a white pigment, an aqueous binder and other components.

Examples of the white pigment contained in the backcoat layer include inorganic white pigments such as precipitated calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminum hydroxide, alumina, lithopone, zeolite, hydrolyzed halloysite, magnesium carbonate and magnesium hydroxide, and organic

pigments such as styrene-base plastic pigment, acryl-base plastic pigment, polyethylene, microcapsule, urea resin and melamine resin.

Examples of the aqueous binder contained in the backcoat layer include water-soluble polymers such as styrene/maleate copolymer, styrene/acrylate copolymer, polyvinyl alcohol, silanol-modified polyvinyl alcohol, starch, cationized starch, casein, gelatin, carboxymethyl cellulose, hydroxyethyl cellulose and polyvinylpyrrolidone, and water-dispersible polymers such as styrene butadiene latex and acryl emulsion. Other examples of the component contained in the backcoat layer include a defoaming agent, a foam inhibitor, a dye, a fluorescent brightening agent, an antiseptic and a water-proofing agent.

To a constituent layer (including the back layer) of the inkjet recording paper or film, a polymer fine particle dispersion may be added. The polymer fine particle dispersion is used for the purpose of improving film properties, for example, stabilizing dimension and preventing curling, adhesion or film cracking. The polymer fine particle dispersion is described in JP-A-62-245258, JP-A-62-136648 and JP-A-62-110066. When a polymer fine particle dispersion having a low glass transition temperature (40°C or less) is added to a layer containing a mordant, the layer can be prevented from cracking or curling. The curling can be prevented also by adding a polymer fine particle dispersion having a high glass transition temperature to the back layer.

The inkjet ink of the present invention can also be used for uses other than the inkjet recording, such as a material for display image, an image-forming material for interior decoration and an image-forming material for outdoor decoration.

Examples of the material for display image include various materials such as poster, wall paper, ornamental goods (e.g., ornament, doll), handbill for commercial advertisement, wrapping paper, wrapping material, paper bag, vinyl bag, package material, billboard, image drawn on or attached to the side face of traffic (e.g., automobile, bus, electric car), and clothing with a logo. In the case of using the dye of the present invention as a material for forming a display image, the image includes not only a strict image but also all patterns by a dye, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

Examples of the material for interior decoration include various materials such as wall paper, ornamental goods (e.g., ornament, doll), luminaire member, furniture member and design member of floor or ceiling. In the case of using the dye of the present invention as a material for forming an image, the image includes not only a strict image but also all patterns by a dye, which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

Examples of the material for outdoor decoration include various materials such as wall material, roofing material, billboard, gardening material, outdoor ornamental goods (e.g., ornament, doll) and outdoor luminaire member. In the case of using the dye of the present invention as a material for forming an image, the image includes not only a strict image but also all patterns by a dye,

which can be acknowledged by a human, such as abstract design, letter and geometrical pattern.

In these uses, examples of the medium on which the pattern is formed include various materials such as paper, fiber, cloth (including non-woven fabric), plastic, metal and ceramic. Examples of the dyeing form include mordanting, printing and fixing of a dye in the form of a reactive dye having introduced thereinto a reactive group. Among these, preferred is dyeing by mordanting.

In the production of the inkjet ink of the present invention, ultrasonic vibrations may be added, for example, in the step of dissolving additives such as dye.

The ultrasonic vibration is added so as to prevent the ink from generation of bubbles due to a pressure applied in the recording head. More specifically, an ultrasonic energy equal to or greater than the energy imposed in the recording head is previously applied in the process of producing the ink to eliminate the bubbles.

The ultrasonic vibration is usually an ultrasonic wave having a frequency of 20 kHz or more, preferably 40 kHz or more, more preferably 50 kHz or more. The energy added to liquid by the ultrasonic vibration is usually 2×10^7 J/m^3 or more, preferably 5×10^7 J/m^3 or more, more preferably 1×10^8 J/m^3 or more. The time period where the ultrasonic vibration is applied is usually on the order from 10 minutes to one hour.

No matter when the step of adding ultrasonic vibrations is performed, the effect can be attained as long as it is after the dye is charged into a medium. The effect is also provided even by adding ultrasonic vibrations after the finished ink is once stored. However, the ultrasonic vibration is preferably added at the time of dissolving and/or dispersing the dye in a medium, because the effect of removing bubbles is large and the dissolution and/or dispersion of dye in a medium is accelerated by the ultrasonic vibration.

That is, the step of adding at least ultrasonic vibrations can be performed during or after the step of dissolving and/or dispersing the dye in a medium. In other words, the step of adding at least ultrasonic vibrations can be arbitrarily performed once or more after the preparation of ink until the ink is finished as a product.

As a practical mode, the step of dissolving and/or dispersing the dye in a medium preferably comprises a step of dissolving the dye in a partial medium out of the entire medium and a step of mixing the remaining medium. The ultrasonic vibration is preferably added at least in either one of these steps, more preferably in the step of dissolving the dye in a partial medium out of the entire medium.

The step of mixing the remaining solvent may be a single step or a multiple step.

In the production of the ink, degassing under heating or degassing under a reduced pressure is preferably used together, because the effect of eliminating bubbles in the ink is enhanced. The degassing step under heating or reduced pressure is preferably performed simultaneously with or after

the step of mixing the remaining medium.

Examples of the ultrasonic vibration-generating device for use in the step of adding ultrasonic vibrations include known devices such as ultrasonic disperser.

In producing the inkjet ink of the present invention, the step of removing dusts as a solid content by filtration, which is performed after the preparation of ink solution, is important. This operation is performed by using a filtration filter and the filtration filter used here is a filter having an effective size of 1 μm or less, preferably from 0.05 to 0.3 μm, more preferably from 0.25 to 0.3 μm. As for the construction material of the filter, various materials can be used, however, in the case of an ink using a water-soluble dye, a filter produced for aqueous solvents is preferably used. In particular, a filter made of a polymer material, which less generates wastes, is preferred. The filtration may be performed by feeding and passing the solution through a filter and may be performed either under pressure or under reduced pressure.

After the filtration, air is often taken in into the solution. Bubbles ascribable to this air give rise to the disorder of image in the inkjet recording in many cases and therefore, the above-described bubble-eliminating step is preferably provided separately. For the elimination of bubbles, the solution after filtration may be allowed to stand or various methods such as ultrasonic defoaming or reduced-pressure defoaming using a commercially available device may be used. In the case of ultrasonic defoaming, the bubble-eliminating operation is preferably performed for 30 seconds to 2 hours, more preferably on the order from 5 minutes to one hour.

This operation is preferably performed in a space such as clean room or clean bench so as to prevent mingling of dusts at the operation. In the present invention, this operation is preferably performed in a space having a cleanness degree of class 1,000 or less. The "cleanness degree" as used herein indicates a value measured by a dust counter.

In the invention, the hitting volume of ink on a recording material is preferably from 0.1 to 100 pl, more preferably from 0.5 to 50 pl, particularly preferably from 2 to 50 pl.

The invention is not limited as for the inkjet recording system and can be used for a known system, for example, an electric charge controlling system of ejecting the ink by using the electrostatic induction force, a drop-on-demand system (pressure pulse system) utilizing an oscillation pressure of a piezoelectric element, an acoustic inkjet system of converting electric signals into acoustic beams, irradiating the beams on the ink and ejecting the ink by utilizing the radiation pressure, and a thermal inkjet (e.g., Bubble Jet (registered trade mark)) system of heating the ink to form a bubble and utilizing the generated pressure.

The inkjet recording system includes a system of ejecting a large number of small-volume ink droplets of a so-called photo ink having a low concentration, a system of improving the image quality by using a plurality of inks having substantially the same color hue but different in the concentration, and a system using a colorless transparent ink. The hitting volume of ink is

controlled mainly by a printer head.

For example, in the case of a thermal inkjet system, the hitting volume can be controlled by the structure of printer head. Specifically, the ink can be hit in a desired size by changing a size of ink chamber, heating section or nozzle. Also, even in the thermal inkjet system, the ink can be hit in a plurality of sizes by providing a plurality of printer heads different in the size of heating section or nozzle.

In the case of a drop-on-demand system using a piezoelectric element, the hitting volume can be changed by the structure of printer head similarly to the thermal inkjet system, however, by controlling a waveform of driving signals for driving the piezoelectric element, the ink can be hit in a plurality of sizes with printer heads having the same structure as described below.

In the invention, the ejection frequency for hitting the ink on a recording material is preferably 1 kHz or more.

In order to record a high-quality image like a photograph, the hitting density must be 600 dpi (number of dots per inch) or more so that an image having good sharpness can be reproduced by a small ink droplet.

In hitting an ink by a head having a plurality of nozzles, the number of heads which can be driven at the same time is restricted, that is, from several tens to about 200 in the case of a type where a recording paper and a head are moved in the directions orthogonal to each other, and several hundreds even in the case of a type called line head where the head is fixed. This is because the driving electric power is limited or in order to avoid the effect of heat generated in the head on the image, a large number of head nozzles cannot be simultaneously driven. Accordingly, the recording at a high hitting density tends to take a long time, but the recording speed can be increased by elevating the driving frequency.

The hitting frequency can be controlled, in the case of a thermal inkjet system, by controlling the frequency of head-driving signal for heating the head.

In the case of a piezoelectric system, the hitting frequency can be controlled by controlling the frequency of signal for driving the piezoelectric element.

The driving of piezoelectric head is described. The hitting size, hitting speed and hitting frequency are determined in a printer control section based on the signal of an image to be printed, and a signal for driving a printer head is prepared. The driving signal is supplied to the printer head. The hitting size, hitting speed and hitting frequency are controlled by the signal for driving the piezoelectric element. Specifically, the hitting size and hitting speed are determined by the shape and amplitude of the driving waveform, and the hitting frequency is determined by the cycle period of signal.

When the hitting frequency is set to 10 kHz, the head is driven every 100 micro-seconds and one-line recording is completed in 400 micro-seconds. When the transportation speed of recording

paper is set such that the recording paper moves 1/600 inch, namely, about 42 micron per 400 micro-seconds, the printing can be performed at a speed of one sheet per 1.2 seconds.

With respect to the constitution of printing apparatus or printer using the inkjet ink of the invention, embodiments discribed, for example, in JP-A-11-170527 are suitably used. With respect to the ink cartridge, embodiments discribed, for example, in JP-A-5-229133 are suitably used. With respect to the suction and the constitution of cap or the like covering the printing head at the suction, those described, for example, in JP-A-7-276671 are suitably used. In the vicinity of head, a filter for eliminating bubbles as described in JP-A-9-277552 is suitably provided.

Also, the surface of nozzle is suitably subjected to a water repellent treatment described in Japanese Patent Application No. 2001-16738. The invention may be used for a printer connected to a computer or for an apparatus specialized for printing of photograph.

The inkjet ink of the invention is preferably used by hitting on a recording material at an average hitting speed of 2 m/sec or more, more preferably 5 m/sec or more.

The hitting speed is controlled by controlling the shape and amplitude of the waveform for driving the head.

Furthermore, by using a plurality of driving waveforms and selecting appropriate waveforms, the ink can be hit in a plurality of sizes with the same printer head.

[Example]

The present invention will be described in more detail with reference to the following examples, but the invention should not be construed as being limited thereto.

EXAMPLES

Ultrapure water (resistively: 18 MΩ or more) was added to the components shown in Table 1 below to make 1 liter, followed by stirring for 1 hour under heating at 30 to 40°C. Then, the solution was filtered under a reduced pressure through a microfilter having an average pore size of 0.25 μm to prepare each ink solution thereby preparing Ink Set 101.

Table 1: Composition of Ink Set 101

	C	LC	M	LM	Y	DY	Bk
Dye	C-1 45g	C-1 15g	M-1 30g	M-1 10g	Y-1 30g	Y-1 30g C-1 3g M-1 5g	Bk-1 55g Bk-2 15g
BTZ	3g	3g	3g	3g	3g	3g	3g
UR	12g	5g	10g	5g	10g	15g	17g
DGB	-	-	-	-	130g	125g	120g
TGB	150g	140g	120g	120g	-	-	-
DEG	100g	100g	90g	80g	-	-	-
TEG	-	-	-	-	110g	125g	100g
GR	120g	130g	130g	120g	125g	135g	125g
PRD	35g	35g	-	-	-	-	35g
TEA	10g	10g	10g	10g	10g	10g	10g
PRX	1g	1g	1g	1g	1g	1g	1g
SW	10g	10g	10g	10g	10g	10g	10g

BTZ: Benzotriazole

UR: Urea

DGB: Diethylene glycol monobutyl ether

TGB: Triethylene glycol monobutyl ether

DEG: Diethylene glycol

TEG: Triethylene glycol

GR: Glycerin

PRD: 2-Pyrrolidone

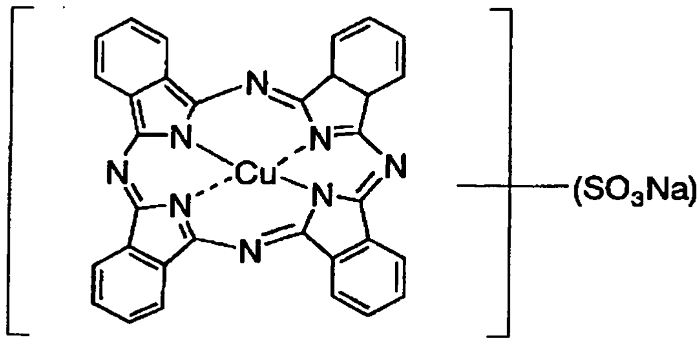
TEA: Triethanolamine (TEA)

PRX: Proxel XL2 (S) (manufactured by Avecia Ltd.)

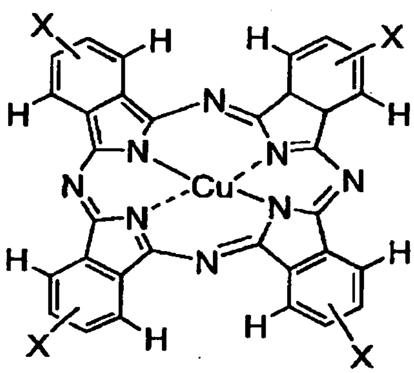
SW: Surfynol STG

Structures of the cyan, magenta, yellow and black dyes shown in Table 1 and Table 2 below are illustrated below.

C-1

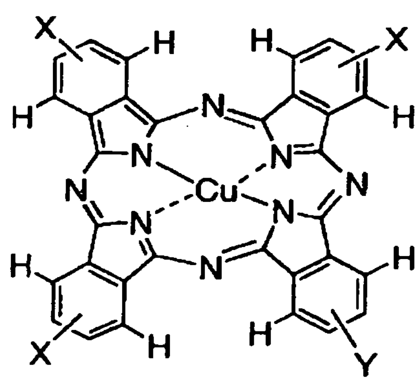


C-2



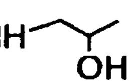
X= $^{-}SO_2(CH_2)_3SO_3Li$

C-3

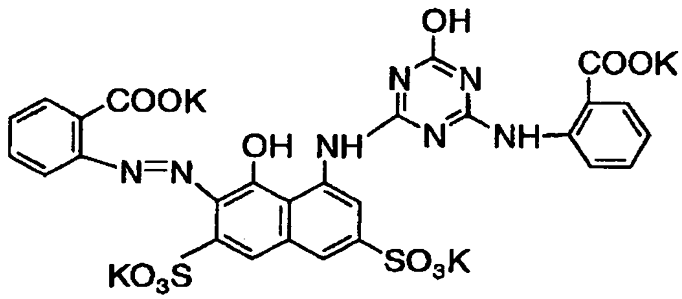


X= $^{-}SO_2(CH_2)_3SO_3Li$

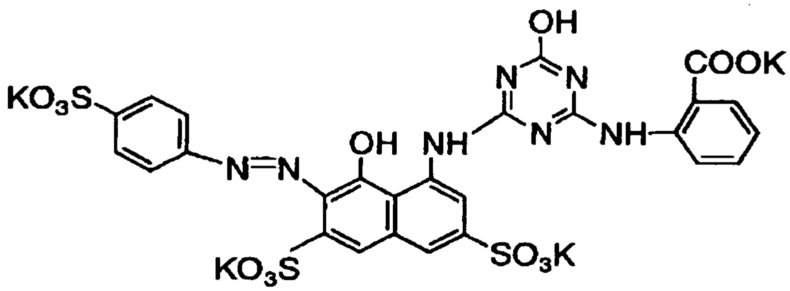
Y= $^{-}SO_2(CH_2)_3SO_2NH$



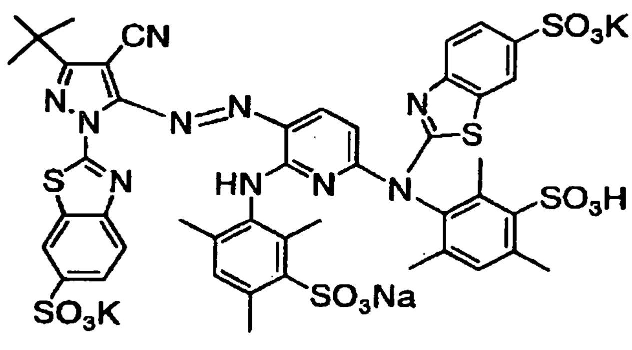
M-1



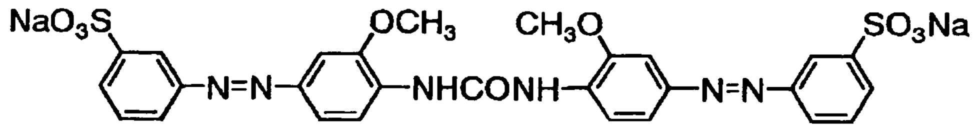
M-2



M-3

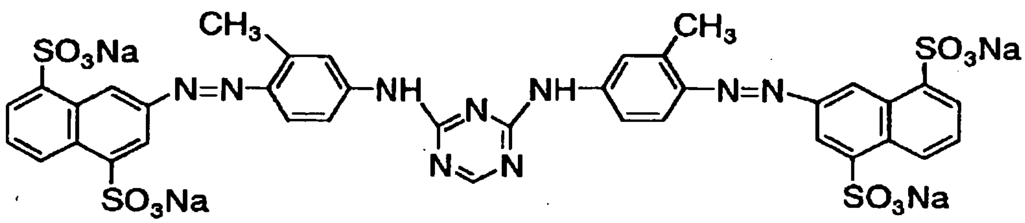


Y-1



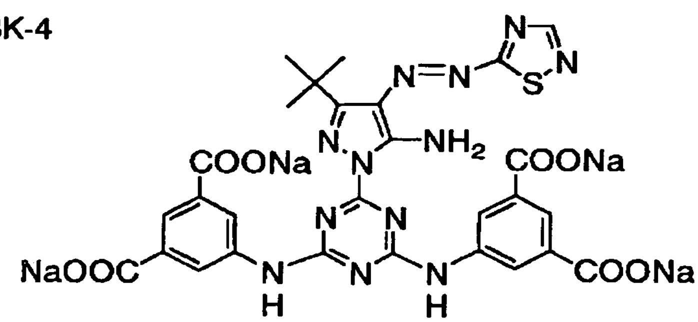
Y-2

BK-2

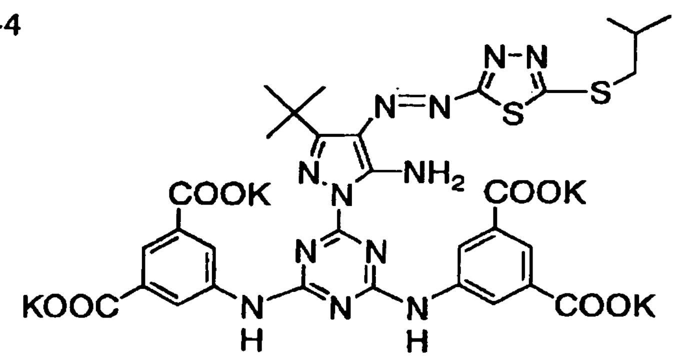


Y-3

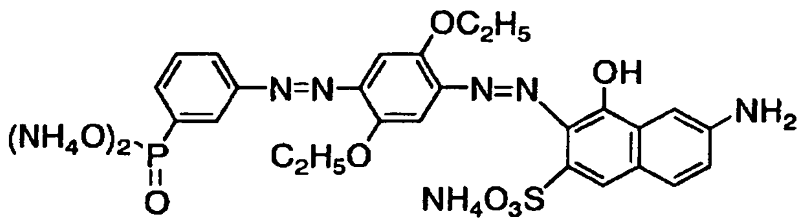
BK-4



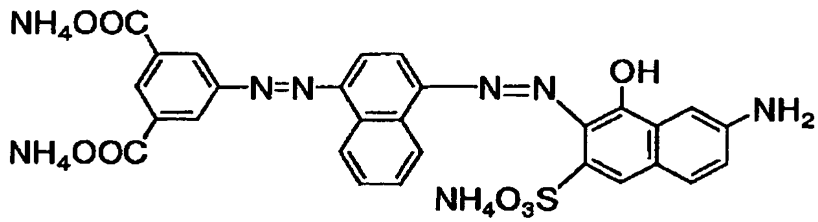
Y-4



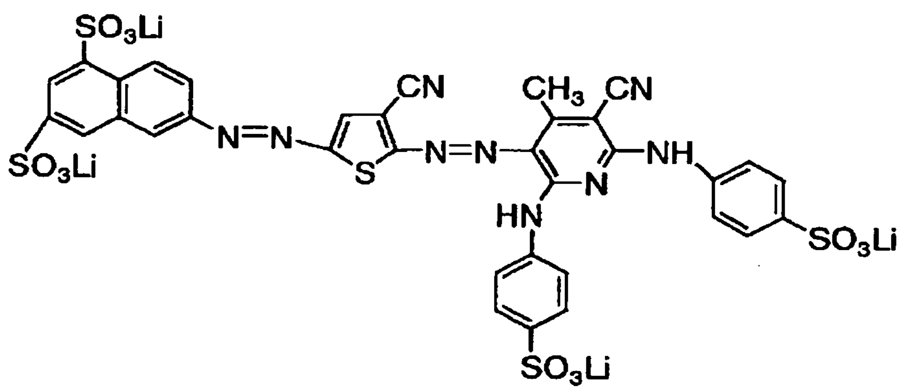
BK-1



BK-3



BK-5



Ink Sets 102 to 109 were prepared in the same manner as in Ink Set 101 except for changing the dyes shown below, respectively.

Table 2

	C	LC	M	LM	Y	DY	Bk
101 (Comparative Example)	C-1	C-1	M-1	M-1	Y-1	Y-1 C-1 M-1	Bk-1 Bk-2
102 (Comparative Example)	C-1	C-1	M-2	M-2	Y-1	Y-1 C-1 M-2	Bk-1 Bk-2
103 (Comparative Example)	C-1	C-1	M-1	M-1	Y-2	Y-1 C-1 M-1	Bk-1 Bk-2
104 (Comparative Example)	C-1	C-1	M-2	M-2	Y-2	Y-1 C-1 M-1	Bk-1 Bk-2
105 (Invention)	C-2	C-2	M-3	M-3	Y-3	Y-3 C-2 M-3	Bk-3 Y-3
106 (Invention)	C-2	C-2	M-3	M-3	Y-3	Y-3 C-4 M-4	Bk-4 Y-3
107 (Invention)	C-2	C-2	M-3	M-3	Y-3	Y-4 C-3 M-3	Bk-3 Bk-4 Y-3
108 (Invention)	C-3	C-3	M-3	M-3	Y-4	Y-3 C-2 M-3	Bk-3 Bk-4 T-4
109 (Invention)	C-3	C-3	M-3	M-3	Y-4	Y-4 C-2 M-3	Bk-3 Bk-5 Y-4
110 (Invention)	C-3	C-3	M-3	M-3	Y-4	Y-3 C-3 M-3	Bk-3 Bk-5 Y-4

With each of the dyes used in the inks, an aqueous solution of the dye having a concentration of 0.1 mmol/liter was prepared and a molar extinction coefficient (ε1) was determined from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring the aqueous solution using a cell having a light pass length of 1 cm. Also, an aqueous solution of the dye having a concentration of 0.2 mmol/liter was prepared and a molar extinction coefficient (ε2) was determined from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring the aqueous solution using a cell having a light pass length of 5 μm. C-1, M-1, M-2, Y-1, Y-2, Bk-1 and Bk-2 exhibit the ratio of molar extinction coefficient lower than 1.2 that is the critical point according to the invention. On the other hand, C-2, C-3, M-3, Y-3, Y-4, Bk-3, Bk-4 and Bk-5 exhibit the ratio of molar extinction coefficient more than 1.2.

The inks were filled in ink cartridges of inkjet printer PM-950C manufactured by Seiko Epson Corp. and a gray stepwise image pattern and a portrait were printed on an image-receiving sheet.

As the image-receiving sheet, Inkjet Paper Photo Gloss "Gasai" manufactured by Fuji Photo Film Co., ltd. was used. With the printed image, image quality, ejection property of ink and image fastness were evaluated.

(Evaluation Experiments)

1) With respect to the ejection stability, the cartridges were set on the printer, ejection of the ink from all nozzles were confirmed, then the printer was stopped and allowed to stand for 240 seconds under conditions of 15°c and 30% RH or conditions of 35°c and 90% RH, and thereafter 100 sheets of A4 size image were output. The outputs were evaluated according to the following criteria:

A: disturbance of printing was not occurred from start to finish of the printing.

B: some outputs having disturbance of printing occurred.

C: disturbance of printing occurred from start to finish of the printing.

2) With respect to the image fastness, printed samples were evaluated in the following manner. The printed sample was prepared by printing cyan and gray patterns changed stepwise in the density. Of these patterns, a pattern having a density of 1.0 ± 0.1 measured using a Status A filter (a Status A green filter in case of printing region with black ink) by X-rite Densitometer was used as the index for measurement of density in the fading test.

(1) In the evaluation of light fastness, the image sample was irradiated with xenon light (85,000 lux) for 7 days using a weather meter manufactured by Atlas Electric Co., Ltd. and then the remaining image density was measured.

(2) In the evaluation of heat fastness, the image sample was stored for 10 days under conditions of 80°C and 70% RH and then the remaining image density was measured.

(3) In the evaluation of ozone resistance, the image sample was allowed to stand for 7 days in a box set to an ozone gas concentration of 0.5 ppm and then the remaining image density was measured.

In each of the evaluations, the image sample wherein the remaining image density was more than 85% of the initial density was rated A, the image sample wherein the remaining image density was from 70 to 85% of the initial density was rated B, and the image sample wherein the remaining image density was less than 70% of the initial density was rated C.

The results obtained are shown in Table 3 below.

Table 3

No.	Ejection Stability	Light Fastness	Heat Fastness	Ozone Fastness
PM-950C (Reference example)	A	B	B	C
101 (Comparative example)	A	C	B	C
102 (Comparative example)	A	C	B	C
103 (Comparative example)	A	C	B	B
104 (Comparative example)	A	C	C	B
105 (Invention)	A	A	A	A
106 (Invention)	A	A	A	A
107 (Invention)	A	A	A	A
108 (Invention)	A	A	A	A
109 (Invention)	A	A	A	A

From the results shown in Table 3 above, Ink Sets 105 to 110 using the dye exhibiting the scale of the concentration dependency of molar extinction coefficient, $\varepsilon 1/\varepsilon 2$, of not less than 1.2 according to the present invention are superior to Ink Sets 101 to 104 for Comparative Examples and Ink Set of Reference Example in all properties of the light fastness, heat fastness and ozone fastness.

[Advantage of the Invention]

The inkjet ink containing a dye having concentration dependency of the molar extinction coefficient as described in the specification and the inkjet ink set including the inkjet ink as a constituting ink according to the invention exhibits excellent ejection stability at the drawing and provides an drawing image having an excellent image durability. Particularly, the ink and ink set exert excellent effects on the inkjet recording use.

[Designation of Document] Abstract

[Abstract]

[Problem] To provide an inkjet ink of an aqueous medium, which exhibits excellent image durability to maintain good image quality of the drawing image after preservation for a long period of time, and an ink set containing the ink.

[Means for Resolution] An inkjet ink comprising at least one dye dissolved in an aqueous medium, wherein the dye satisfies a relation of $\varepsilon 1/\varepsilon 2 > 1.2$ wherein $\varepsilon 1$ represents a molar extinction coefficient obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.1 mmol/liter using a cell having a light pass length of 1 cm and $\varepsilon 2$ represents a molar extinction coefficient obtained from absorbance at the maximum wavelength of a spectral absorption curve obtained by measuring an aqueous solution of the dye having a concentration of 0.2 mmol/liter using a cell having a light pass length of 5 μm.

[Selected Drawing] None